Addis Ababa Science and Technology University

College of Biological and Chemical Engineering

Department of Environmental Engineering

Defluoridation of Aqueous Solution using Activated Carbon from Catha edulis

By

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I declare that this thesis of M.Sc. degree entitled “Defluoridation of Aqueous solution using Activated Carbon from *Catha edulis*” is submitted by me to the Addis Ababa Science and Technology University. This paper is my original work and has not previously been submitted to other universities, organization, or institutes.

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Abstract

The adsorption process of the activated carbon adsorbent produced from *Catha edulis* stems was conducted in order to remove fluoride from aqueous solution. Activated carbon of *Catha edulis's* stems was prepared by activating using chemicals (H_2SO_4, H_3PO_4, and KOH) and temperature (500°C, 550°C, and 600°C). The produced activated carbons were characterized for better adsorbent and as a result processing with KOH at 550°C AC was selected. In the adsorption batch process, it was conducted with selected activated carbon using three factors with three levels; pH (2, 6.5, and 9), dose (0.5, 1.0, and 1.5 g/L), and contact time (60, 90, and 120 min.). After the experimental procedure, the better adsorption of fluoride removal efficiency was found at pH 2 using 1.5 g/L of adsorbent within an hour. Removal efficiency was obtained at an average of 72.4%. Fluoride adsorption seemed to increase when the amount of adsorbent increased from 0.5 to 1.5 g/L. Interaction effects of factors and its level was obtained using Minitab 17 software and the overall of the two-way (P=0.000) and three-way (P=0.013) interaction of the total average showed that the effects were significant. By looking in details, two-way interaction between dose*pH have more significant P-values than dose*time and pH*time. The Three-way interaction shows less significant P-values. Hence, this showed that the factor (time) has less effect when it interact with the other factors. In adsorption isotherm, both Langumuir and Freundlich isotherm model were studied and the fluoride adsorption model was found to be better fitted using the Freundlich isotherm model (R^2=0.98). Adsorption kinetics was also studied by using both pseudo first and second order equations. So the better fit for the fluoride adsorption was well obtained at second order kinetics. Fixed bed column continuous flow was executed and a good adsorption obtained from 30 min. up to 4 hrs. (93% to 89%). Then after 10 hours of continuous flow adsorption, the adsorbent was exhausted and the removal fluoride concentration efficiency becomes negligible.

Keywords: Defluoridation, activated carbon, *Catha edulis*, adsorption, adsorption kinetics, adsorption isotherm.

ABBERIVATION

AA	Activated Alumina
ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance
AC	Activated Carbon
FTIR	Fourier Transform Infrared Spectroscopy
EDTA	Ethylenediaminetetraacetic acid
CDTA	Eyclohexanediaminetetraacetic acid
TISAB	The ionic strength adjustment buffer
PPM	Parts per million
WHO	World Health Organization
MWIE	Ministry of Water, Irrigation, and Energy

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1. INTRODUCTION

1.1. Background

Water is one of the basic necessities for human being; however, developing countries have a problem of accessing clean water. Water covers almost ¾ of the earth's surface. However, most of it is salinized and contains toxic substance like arsenic, leads, chromium, manganese, fluoride, and others which cause health disorder if used as drinking water. Contamination could be obtained from nature or industrial effluent. Water bodies around the world contain fluoride concentration with more than 1.5 mg/L (WHO, 2004). The high concentration of fluoride in water creates a major problem in drinking water supply. In the early 1980s, it was estimated that around 260 million people worldwide were drinking water with more than 1 mg/L of fluoride (Frencken, 1992). Countries like China, India, Mexico, Argentina, and East African countries (Sudan, Ethiopia, Uganda, Kenya, and the United Republic of Tanzania) are recognized with high level of fluoride (WHO, 2004).

Fluoride in both surface and ground water originates mainly from natural minerals in the rocks and minerals/soils with which water interacts (Jagtap et al., 2012). It is mostly based on basement aquifers, granites, volcanic rocks and geothermal sources deposit, weathering, dissolution of minerals and sedimentary aquifer particularly in arid areas (Smedley et al., 2002). Fluoride ions can also be found in effluents from semiconductor, metal processing, fertilizers, and glass-manufacturing industries. The discharge of such wastewater into the water surface would lead to increased levels of fluorides in surface and groundwater (Chaturvedi et al., 1990). Fluorine is a lightest of the halogen element that does not occur in the elemental state in nature but as a fluoride because of its high reactivity. It accounts for about 0.3 g/kg of the Earth's crust and exists in the form of fluorides in a number of minerals, of which fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) are the most common (WHO, 2004). Apatite ($Ca_5(PO_4)_3$(F, OH, Cl)), Bastnaesite ((Ce, La) (CO_3)F), Sodium fluoride and magnesium fluoride are also found as natural minerals (Smedley et al., 2002).

Depending on the concentration of fluoride, it could have positive or negative effect; it could calcify the teeth in low amount or dental and skeletal fluorosis at high amount. The consumption of fluoride water above 1.5 mg/L causes dental fluorosis and fluoride above 4 mg/L cause skeletal fluorosis. Skeletal fluorosis is a very harmful disease which affects the bone and joint when will result in crippling bones and also damage the nerve system (Tekle-Haimanot, 1987; Dissanayake, 1991).Fluoride has a very high tendency to get attracted by positively charged ions like calcium. Hence, the effect of fluoride on mineralized tissues like bone and teeth could be beneficial or detrimental depending on their concentration. Fluoride concentration between 1.0 and 1.5 mg/L could be beneficial to young children for calcification of dental enamel. The most common health problems associated with the excess fluoride amount in drinking water are dental and skeletal fluorosis (Hillier et al, 2000).

The mild form of dental fluorosis is characterized by chalky white teeth, whereas yellowish brown pigmentation in the middle of the teeth and severe pitting and loss of the teeth is an indication of severe effect of fluorosis. In the early stages of skeletal fluorosis, fluoride gets deposited in joints of shoulder bones, neck and pelvic, and knees and makes it difficult to move, walk and bend causing pains. In the later stages of skeletal fluorosis marked by restriction of spine movements and, hence it can't be easily diagnosed. The advanced stage is osteoporosis involving hardening and calcifying of bones and causes pain, stiffness and irregular bone growth. At its worst conditions, this results in severe bone deformation and debilitation (Frencken, 1992). In a report of WHO (2004) also indicated that a long term consumption could result in DNA destruction, paralysis volition, cancer. The table 1:1 below shows the effect of fluoride during consumption.

Table 1:1 Effect using level of fluoride in drinking water

Concentration of Fluoride (mg/L)	**Effect**
<0.5	Dental caries
0.5–1.5	Optimum dental health
1.5–4.0	Dental fluorosis
4.0–10	Dental and skeletal fluorosis
>10	Crippling fluorosis

(Dissanayake C.B, 1991)

India is one of the countries suffering from fluoride consumption, it was estimated that 25 million people have been affected and 66 million are at risk and deals with fluorosis effect. It was observed that 26% to 84 % of children under 16 year old and 24% to 97% of adult were affected by fluorosis. The fluoride concentration in different parts of India reported to vary from 0.2 mg/L to 48 mg/L (WHO 2004). In Kenya, most of the affected groups are the children with the dental and skeletal fluorosis. Depending on the altitude when it decrease from 1986 to 1500m above sea level and the affected group increases from 36% to almost 94%. Excess fluoride water occurs in Lakes Rudolph (12 mg/L), Hannington (1,100 mg/L), Baringo (6 mg/L), Magadi (1980mg/L), Nairobi (14 mg/L) and Elmentaita (1,640 mg/L) (WHO, 2004). Recordings show that the highest fluoride level was found at Lake Nakuru, Kenya wells 2800mg/L (Kloos and Tekle-Haimanot, 1999). Majority of these people live in tropical countries where the problem is exacerbated by the need to drink more water because of the heat.

The water in the Rift Valley regions of Ethiopia also identified as an area with high fluoride concentration than the other parts of the country. Eastern Shewa Zone (Wolenchiti Woreda) and Southern Afar's groundwater showed with fluoride concentration (20-40 mg/L) (MWIE , 2013). Fluoride concentration varied due to more recent volcanic activity of the Rift Valley and generally higher fluoride levels is in basaltic rock than in surface sediments resulting in discharge of thermal water in to fresh surface water bodies (Baker et al., 1972; Belachew, 1990). Some part of Rift Valley also with high fluoride concentrations like Lake Shalla (177-235 mg/L), Lake Hertale (26 mg/L), and at Sodo Resort have between 6.0 and 22.6 mg/L (Elizabeth et al., 1992; Tamiru, 2000). A study conducted in the Ethiopian Rift Valley areas of Oda, Wonji and Bulbula, found that the fluoride level in drinking water collected from wells ranged from 1.5 to 36.0 mg/L (Sengupta and Pal, 1971; Tekle-Haimanot et al., 1987). There are very high differences in fluoride concentration in Ziway-Shala basin among various water bodies; 1.9 to 250 mg/L for lakes, 2 to 150 mg/L for hot springs, from less than 0.1 to 64 mg/L for boreholes and 2 to 67 mg/L for wells around Langano (Berhanu, 1996; Ayenew, 2008).

In the Rift valley regions, the removal of fluoride (Defloridation) is one of the options to access safe water like in developing countries which suffers in accessing water supply (Malde et al., 2004). Some of the fluoride removal methods are precipitation and adsorption. Precipitation methods like nalgonda technique which involves forming of flocs

with fluoride then after sometime, the flocs start to settles. The membrane filtration method is widely used in developed countries because it requires advanced technology, capital intensive, high energy consumption, and maintenance (Zewge, 2001). Adsorption methods are a process when the water passes through the adsorbent, the fluoride will attached to the surface or interface either by force attraction or by chemical bond. In the adsorption techniques adsorbents like activated carbon, aluminum sulphate, improved clay, and other materials with adsorbing behavior can be employed (Petrusevski, 2012). Activated carbon prepared from plant has been used for centuries for various purposes like odor removal (deodorization), water purification, medicine, and decolorization (Ahmadpour, 1997). Nowadays the uses of activated carbon in the management of environmental pollution becoming a common exercise (Mohammed and Ansari, 2009). It is often applied in the removal of both organic and inorganic species from a drinking water and wastewater treatment (Ferhan and O¨zgu¨r, 2011). Therefore, the use of activated carbon in water treatment is one of the low cost technologies which can be used in defluoridation using wood material for the production of the adsorbent (Ferhan and O¨ zgu¨r, 2011).

1.2. Problem of statement

The Rift valley regions of Ethiopia are the volcanic areas where the ground and surface water contain high amount of fluoride than the recommended concentration below 1.5 mg/L (WHO, 2004). Hence the population in the region exposed to dental and skeletal fluorosis of health problems as a result of consuming high concentration of fluoride water. In order to overcome the health problem associated with dental and skeletal fluorosis the community either to be supplied with fresh water or reduce the level of fluoride in water with low cost technologies. Developing countries having such problems look for adsorption techniques using different adsorbents, particularly an activated carbon produced from biomass or agricultural waste. In Ethiopia one of the major problems in cities is the use of *Catha edulis* and discarding the unusable part. *Catha edulis*'s stems are considered as a waste material and get disposed of everywhere especially around the chat market areas, streets, and dumpsters.

Previous studies conducted on fluoride removal using various adsorbent like aluminum hydroxide, activated alum, bone char, clay, wheat straw, sawdust, and activated bagasse carbon, and other adsorbents (Asheesh et al., 2012; Chauhan et al.,2007; Nahum et al.,

2007). In this study activated carbon derived from *Catha edulis* produced by chemical and activation process was tested using 30 mg/L as initial fluoride concentration. The selection of fluoride concentration based on the water sources in areas like Wolenchiti Woreda and southern Afar with more than 20 mg/L (20-40 mg/L) of fluoride. The research result might contribute to the reduction options associated with the problem of fluoride concentration in water source for possible and feasible use, and as an alternative method for defluoridation treatment. Nevertheless, knowledge on activated carbon production will be enhanced and disseminated.

1.3. Scope of work

The scope of the work includes production of activated carbon using *Catha edulis's* stems, screen out the best adsorbent production parameters, and finally conduct the fluoride removal in an aqueous solution using batch adsorption process from the selected activated carbon, evaluating adsorption's kinetics and isotherm to understand rate adsorption.

1.4. Objective

Main objective

The main objective is to investigate removal efficiency of fluoride from aqueous solution using activated carbon developed from chat's stems (*Catha edulis*).

Specific objective

- To characterize, and screening of best the activated carbon produced by using various temperatures and activating chemicals,;
- To determine fluoride removal efficiency of screened activated carbon at different factors (pH, contact time, and dosage)
- To evaluate adsorption isotherms and kinetics using selected factor;

2. LITREATURE REVIEW

Many part of the world have been recognized with high fluoride concentration particularly India, China, Sri Lanka, Mexico, western USA, Argentina and many countries in Africa. Fluoride removal by water treatment is carried out in some countries. However, as many of the high-concentration occurs in developing countries, fluoride removal practices vary widely and many high-fluoride water sources are used without treatment. As a result, large populations throughout parts of the developing world suffer the effects of chronic endemic fluorosis. High amount of fluoride in drinking water causes many health problems. Due to this problem potable water in areas with high amount of fluoride should be removed to the recommended level below 1.5 mg/L (WHO, 2004). If the fluoride concentration in the water supply is significantly and consistently beyond the permissible level, it is essential to consider for remedial measures to combat fluorosis. The choice of the defluoridation method depends on conditions like economic status, concentration of fluoride, availability of resources, area, etc. Among all these techniques, adsorption methods have more advantages because of their greater accessibility, economical, ease of operation, and effectiveness in removing fluoride from water (Chauhan et al., 2007; Mohan et al., 2007; Ayoob and Gupta 2008). There are several fluoride removal techniques: Precipitation Method, Adsorption Method, Membrane Method (Petrusevski, 2012; Mariappan and Vasudevan, 2002).

2.1. Precipitation methods

It is a process of water treatment forming insoluble fluoride compounds by adding appropriate reagent (coagulants and coagulant aids)which then be precipitated due time and removed from water (Mariappan and Vasudevan, 2002). Hence, fluoride removal is accomplished with separation of solids from liquid; some of the chemicals used are alum, lime, magnesium, calcium phosphates, and aluminum hydroxyl sulphate in defluoridation by precipitation technique (Nawlakhe et al., 1978; Larsen et al., 1993; Mariappan ad Vasudevan., 2002). The best example of this technique is Nalgonda technique of defluoridation. The procedure include addition of lime and Al coagulant (aluminum sulphate), followed by flocculation, sedimentation, filtration and disinfection processes performed by adding aluminum salt of aluminum sulphate (alum) or aluminum chloride or their combination. In this process the insoluble fluoride salts are formed in to dense flocks

and rapidly settles when using lime. Approximate doses of alum required to obtain water with acceptable limit (<1.0 mg/L) at various fluoride and alkalinity levels in raw water (Petrusevski, 2012). A study using activated and ordinary quick lime for removal of fluoride and was found 80.6% from concentration of 50 mg/L (Islam and Patel, 2007). Hence, the study concluded that it is suitable to remove fluoride from industrial effluent where the concentration is high. But this method cannot be employed to treat water for domestic purpose, since it cannot bring fluoride within the permissible limit. The drawbacks of this technique are the cost of lime and alum, the management of the excess sludge formed (Petrusevski, 2012).

2.2. Membrane method

Membrane is a type of treatment technology for drinking water which is mostly used in developed country due to its high energy requirement, capital intensives and technological advancement (Zewge, 2001). Reverse Osmosis, nanofiltration and electrodialysis are some of the methods which used in membrane process and are claimed to be the best water treatment technology known. The technique achieves more than 90% fluoride removal (Sobsey 2002). The hydraulic pressure in reverse osmosis is applied on one side of the semi permeable membrane forcing the water across the membrane leaving the salts behind. Depending on the pressure exerted on the membrane, the relative size of the pollutants is also left behind. The membranes in electro dialysis permit the ions to pass through except for water. The driving force is an electric current which carries the ions through the membranes (Manjula, 2016). The removal of fluoride reported to vary from 45 to 90 %. The membranes are very sensitive to pH and temperature. The units are also subject to chemical attacks, plugging, fouling by particulate matter, and concentrated and large quantity of wastes (Kumar and Gopal, 2000).

2.3. Adsorption method

Principle of adsorption

Adsorption is a process by which molecules can adhere on a substance in homogenetic or heterogenetic phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid surface or interfaces. The basic principle of adsorption is due to mass transfer and molecule adsorption from liquid or gas in to solid surface. It involves the inter-phase accumulation of substance on a surface of interface. The bulk concentration being adsorbed is the

adsorbate and the material which adsorption takes place is the adsorbent. Adsorption influences the distribution of the substances which in turns affects their transport. It also affects the electrostatic properties which in turn influences their tendency to aggregate and attach and the reactivity of the surface (Sharma, 2012).

Types of adsorption

The active force within the phases of surface boundaries' energy results in the attraction forces between molecules, which would be accumulated forming layers. There are two primary forces type of adsorption called Physical and chemical adsorption. The hydrophobic nature of the substance tends to be adsorbed than staying in the solution and the electrical attraction. The attraction could have occurred due to physical (van der Waals) or chemical interaction with the adsorbent (Ferhan and Ὸzguȓ, 2011). **Physical adsorption** is a process when the force of attraction exists between adsorbate and adsorbent are weak, i.e. Van der Waals forces of attraction. Physical it has low enthalpy of adsorption (20-40 KJ/mol). Adsorption also takes place at low temperature below boiling point of the adsorbate. Physical adsorption does not involve the sharing or transfer of electrons. **Chemical adsorption** is a process when the force of attraction existing between adsorbate and adsorbent are chemical forces forming chemical bond. It has high enthalpy of adsorption. The adsorbed molecules are localized on specific sites and therefore are not free to migrate about the surface (Sharma, 2012).

Adsorption on a solid is influenced by a number of factors such as, surface area, nature of the adsorbent, hydrogen ion concentration (pH) of the solution, temperature, mixed solutes and nature of adsorbate (Sharma, 2012). These methods are preferable because of the sludge production is very low, it easy to operate and maintenance, and can be processed in a very low cost. The adsorbent ability is dependent on the pore size, pore size distribution, and functional groups which are the main reasons for adsorption occurrence. The functional groups on the surface of the adsorbent such as amino, carboxyl, thiol, alcohol, phenol, and phosphate groups could affect the adsorption phenomena. The surface of the adsorbent particles can be modified to improve the fluoride adsorptive capacity. Such modifications have been brought about by creating new functional groups which have strong affinity for fluorides. Modification of the structure of an activated product can be conducted by using activating chemical agent, steam pyrolysis or both to produce activated material for fluoride ion adsorption (Daifullah et al., 2007). The adsorption

process can be developed depending on the economic cost, high potential of the adsorption, effectively, technicality, efficiently and low time (Sharma, 2012). Some of the widely used and investigated adsorbents are mentioned below:-

2.3.1. Activated alumina

Activated alumina (AA) is an adsorbent in which ions in solution are adsorbed on the oxide surface (Thomas and Crittenden, 1998). AA has large surface area and high adsorption capacity which is independent to temperature. Studies using AA on fluoride removal showed as an effective method by removing above 85% and it depends on pH. The disadvantage of this method is that AA adsorbs bicarbonate ions which will reduce absorbability of the fluoride ions and competes for the surface area of activated aluminum oxide. In addition to this, if the exhausted AA is not regenerated, the cost of deflouridation become high, and the management of the regenerated wastes is also a problem (Petrusevski, 2012).

2.3.2. Clay

Clays are available, sustainable, and economical raw material that can be used in adsorption of substances. The pore size and surface area of the clay can be enhanced by treating with pH, contact time, and temperature. It is relatively inexpensive and can be used for re-refining edible and mineral oils, adsorbing toxic chemicals, removing pigments, etc. The cationic forms are capable of adsorbing a range of polar molecules and non-polar molecules (Ferhan and Özguŕ, 2011). Studies conducted using different kinds of clay showed variation in their adsorption potential and the outcome of the experiment was successful with varying composition of Al and Fe ranging from 5% to 85% in clay (Ahmedin, 2007). And depending on the source of the clay there may exists heavy metals and other pollutants which could cause harm and require pretreatment for the removal of these substances (Fawell et al. 2006).

2.3.3. Activated carbon

Activated carbon is an amorphous carbon material (animal, plant) which are prepared by using thermal (burning) or chemical addition or both in a way that degree of porosity and surface area increased and the carbon surface oxidized (AbdulHalim et al, 2000). Activated carbon is a non-hazardous, processed, carbonaceous product, having a porous structure with large internal surface area. These materials can adsorb a wide range of

substance, of non-carbon impurities usually used for gas and water treatment (Bansal and Goyal, 2005). It is the most widely used adsorbent since most of its chemical (e.g. surface groups) and physical properties (e.g. pore size, distribution, and surface area) can be modified. The wide application of activated carbon is derived from its large micropore (and sometimes mesopore) volume and the resulting high surface area (Bansal et al, 1988). The production of activated carbon performed in two methods: the physical activation and chemical activation methods.

Physical activation

The basic characteristics of carbon are established during the pyrolysis, and the ensuing oxidation step must be designed to complement the pyrolysis step. During this step, the oxidizing agent increasingly erodes the internal surfaces of the carbon, develops of pores in the carbon, and changes the surface to specific chemical forms which may have selective adsorption capabilities (Bansal et al., 1988). Activation temperature, steam, and CO_2 flow rates control the pore development, which in turn affect the pore size distributions and the level of activity of the activated carbon (Smíšek and Černý, 1970). It is generally carried out at elevated temperatures between 700°C and 1100°C in the absence of air in order to produce activated carbon (Ferhan and Özguř, 2011). This process eliminates most of the non-carbon elements such as hydrogen, nitrogen, oxygen and sulphur as volatile gaseous products (Balci, 1992).

Low molecular weight volatiles are first released, followed by light aromatics and finally the hydrogen gas, the resultant product being a fixed carbonaceous char. The residual carbon atoms are grouped into condensed sheets of aromatic ring with a cross-linked structure in a random manner. The mutual arrangement of these aromatic sheets is irregular and leaves free interstices between the sheets, which may be filled with the tarry materials (Smíšek and Černý, 1970). The moisture content, heating of the system and the temperature of carbonization of the starting material can significantly affect rate of pyrolysis. If the materials are carbonized in a simple form product, the crystallites would be irregular. This results in deposition and decomposition of tarry substances, which will be filled or blocked by disorganized (amorphous) carbon. Hence the carbonized product has small adsorption capacity, the tar remains in the pores between the crystallites and on their surface at lower temperatures (Yağşi, 2004).

The carbon is first oxidized the absence of air or limited and controlled oxygen during carbonization and activation processes. The activation of charcoal consists in thermal treatment at high temperatures (400°-1100°C); as a result, these incomplete combustion products burn up and volatilize (Hassler, 1963). Then the surface of the carbon is tremendously increased by the removal of hydrocarbon or tars (Lagaude et al., 1988). In such cases, the tarry products can be removed by heating them in a stream of an inert gas, or by extracting them with a suitable solvent or by a chemical reaction (Smíšek and Černý, 1970, 1970; Wigmans, 1989).

Chemical activation

The chemical activation usually takes place at a lower temperature and shorter time than used in physical activation. A very high yield of carbon also obtained in chemical activation because the chemical agents used are substances that reduce the production of other volatile products and it can improve the pore development in the carbon structure (Ahmedpour and Do, 1997). Most carbonaceous substances can be converted into activated carbon; the final properties of the carbon will depend significantly on the nature of the starting material, carbonization, and activation of time and temperature.

Chemical activation is carried out by impregnating the sample material with an activating agent of like phosphoric acid, hydrochloric acid, sulphuric acid, and alkalis mainly KOH (Khalili et al, 2000), then pyrolysis at lower temperature than the physical activation process in the absence of oxygen. Activated carbons produced by chemical activation generally exhibit a very open structure and ideal for the adsorption of large molecules. The degree of impregnation, contact time and temperature are some of the important factors in chemical activation which could affect the porosity of the product (Balci, 1992).

The advantage of chemical activation is that;

- The process normally takes place at a lower temperature and for a shorter time than those used in physical activation.
- Very high surface area activated carbons can be obtained.
- The yields of carbon in chemical activation are high because it involve dehydrogenation properties which hinder formation of tar and reduce the production of other volatile products

- It changes the carbon to a better skeleton by the creation of a porous structure and surface area.

The quality of activated carbon is influenced by the raw material and the activation procedure are involved for enhancement of the chemical nature of the surface oxides and the surface area of the final product, the nature of the starting material are very important. Any cheap matter with a high carbon and low ash content can be used as a raw material. The raw materials used to produce activated carbon include (carbonaceous materials) fish and cattle's bone, egg shells, wood, peat, brown coal, bituminous coal, lignite, coconut shells, almond shells, pits from peaches and other fruit (Balci, 1992).

Bone char is one of the most oldest and low cost method, simple to use and locally available. The preparation of bone charcoal to be carried out in a properly designed kiln or furnace in order to control extremely unpleasant smell and taste even in a spacious rural environment(Nahum et al, 2007). Researches have been conducted in order to determine the effects of solution pH and temperature on the adsorption of fluoride onto bone char (Nahum A. et al, 2007). Fluoride adsorption capacities among several adsorbents revealed that the adsorption capacity of the bone char was greater than those of commercial products of activated alumina and activated carbon. The adsorption capacity is considerably dependent upon the physicochemical properties of the bone char surface and the solution pH. The bone char is dominated with mesoporous size adsorbent of a high surface area. The adsorption capacity of bone char increased drastically when the solution becomes an acidic; this behavior was due to electrostatic interactions between the F- anions in water solution and the charge of the bone char surface (Larsenet al., 1993).

In selection of the raw materials for activated carbon production, that the raw material should be high in carbon content, low in inorganic content (i.e low ash), sustainability of the raw material and inexpensive (Smíšek andandand Černý, 1970; Elliot, 1981; Holden, 1982). Wood char is one of the raw materials widely used for activated carbon biomass resource (Ferhan and O¨zgu¨r, 2011). Wood char is one of the cheapest, simplest, easily available and accessible can be used for defluoridation in developing country (Kumar et al, 2007). Charcoal has some adsorption capacity, but this is greatly enhanced by the activation process (Cheremisinoff, 2002). Different plant parts (seeds, leafs, roots, and woods), as natural adsorbent were tried as defluoridation agents. The roots of Vetiver

grass (*Vetiveria zizanoides*) were tested as an adsorbent and found to be an effective defluoridation and could remove as much as 70% of the fluoride from a sample. Tamarind seeds were also successfully tested for defluoridation by sorption and considered as a kitchen- waste, which can be obtained at much cheaper price (Murugan and Subramanian, 2006). Studies have been conducted using activated carbon produced from neem and kikar leaves to remove nearly about 80% of fluoride. Both leaves were sieved to obtain a particle size of 0.3 and 1mm. The batch experiment was conducted with different parameters (pH, adsorbent dose, and contact time) to investigate the adsorption efficiency of activated carbon produced from different biomaterials. Hence the result differs depending on the parameters and the best adsorbent was found to be activated kikar carbon. The activated carbon adsorption rate, capacity and efficiency was affected by using different amount of dosage, pH level and contact time (Kumar et al, 2007).The surface of the carbon ions differ depending on the pH value until the adsorption reached to its limit. (Mohammed and Ansari, 2009).

Materials like granular activated carbon from corn cob and *Acacia nilotica* stalk by KOH activation carbonized at 800°C was used in batch study for defluoridation of water and was found an adsorption for corn cob activated carbon81% and for *Acacia nilotica* stalk 83%respectively (Shivayogimath et al,2014). Heat activated neem stem charcoal was used for defluoridation of aqueous solution and achieved the removal of 94 % was achieved from 10mg/L of fluoride bearing solution at pH of 5.0 (Chakrabarty and Sarma, 2012). Karthikeyan and Ilango (2007) have used *Morringa indica* bark activated carbon for defluoridation of aqueous solution with contact time of 25 minutes achieved a maximum removal of 80% from 3 mg/L initial fluoride concentration solution at 3g/L dose and pH of 2.0.

2.4. *Catha edulis* stems as a raw material

Khat or in its scientific name *Catha edulis*, is a dicotyledonous evergreen shrub of the family Celastraceae (Kennedy, 2012). The oral traditions claim that khat originated from Yemen; however the literature indicates that khat originated from Ethiopia, specifically in Hararghe with a gradual expansion to different parts of Ethiopia, Yemen and other parts of the world (Huffnagel, 1961). The color appearance (green, brunette, and gray) and strength (smooth, weak, and rough) depends on their type and maturity, geographical

location and branches. Oromia, mainly East and West Hararghe zones, is the most important center of khat production in Ethiopia (Lemessa, 2001). Hararghe is considered to be the most important producer of quality khat in the world (Kennedy, 2012).

Studies on the chemical composition of the extracts of *Catha edulis* leaves identified as a different compound under the group of alkaloids, terpenoids, flavonoids, sterols, glycosides, tannins, amino acids, vitamins, and minerals. The phenylalkylamines and the cathedulins are the major alkaloids and it also contains considerable amounts of tannins (Kalix and Braenden, 1985). Cathinone a phenylalkylamine, is mainly found in the young leaves and shoots, which is a strong potency in stimulating the central nervous system (Al-Hebshi andand Skaug, 2005). Cathinone is unstable and undergoes decomposition reactions after harvesting and during drying or extraction of the plant material and is presumably the main psychoactive component of khat. Its fresh leaves and tops are chewed or, less frequently, dried and consumed as tea, in order to attain a state of euphoria and stimulation (Al-Hebshi and Skaug, 2005). *Catha edulis*'s stems (khat) are one of the wasted and scattered materials in Addis Ababa and Hararghe regions. Khat consumers mostly use only the tip fleshy leaf part of the plant and throw the stems away which is considered as a waste. In addition to that, since this investigation involves wood as an adsorbent, using khat stems is better than cutting trees which will lead to deforestation.

3. MATERIALS AND METHODS

3.1. Materials

Furnace, oven, Fluoride meter (HI 98401), magnetic stirrer, sieve mesh, funnel, filter paper, conical flask, test jars, pH meter (model 3305), mortar and pestle, pipettes, and electronic balance (BSA2245-CW). The uses of these materials will be well explained in the experimental section.H_2SO_4, KOH, and H_3PO_4 were used as an activating agent to produce activated carbon. HCl and $NaHCO_3$ were used to wash the activated sample. HNO_3 and NaOH were used to adjust pH media. The ionic strength adjustment buffer (TISAB) was also prepared by following a recommended procedure, except that EDTA (ethylenediaminetetraacetic acid) replaced CDTA (cyclohexane diaminetetraacetic acid) (Baily, 1980).

3.2. Methods

Stock solution (1000 mg/L) was prepared by diluting 2.21g of NaF salt powder to 1000 ml of deionized water. Then standard solution (30 mg/L) was prepared by diluting stock solution with deionized water. A 100 mg/L and 10 mg/L solutions were also prepared to calibrate the fluoride electrode.

3.2.1. Preparation of activated carbon

Unusable stem of *Catha edulis* was collected from Merkato called chat tera in Amharic, Addis Ababa. The collected raw material was washed, dried with distilled water to remove foreign material and reduced /cut in to size of 10 mm. The selection of this size is based on different literatures reports from different plant materials (Ferhan and O¨zgu¨r, 2011; Mao. et al, 2015). The chips were impregnated in chemicals (KOH, H_2SO_4, and H_3PO_4) for 24 hr. to activate the raw material in order to achieve good carbon structure and surface area (Jagtoyen and Derbyshive, 1998; Khalili et al, 2000; Hameed et al, 2007; Solum et al, 1995).

Then the samples was washed with distilled water and heated at 110^{o}C to dryness in an oven for 3 hours. Based on the literature the impregnated samples were pyrolysised at three different temperatures 500°C, 550°C and 600°C for 1 h in a muffle furnace (Werku N. et al., 2007; Shivayogimath, et al., 2014; İlknur and Canan, 2016).

The activated carbons were washed thoroughly with 3N HCl and were heated to 40^{o}-50^{o}C to solubilize the mineral (Shivayogimath, et al., 2014). The activated carbon produced from (H_2SO_4 and H_3PO_4) was also washed with 1% $NaHCO_3$ solution to remove residual acid (Asheesh et al., 2012). Then finally the activated carbon was washed with deionized water till it reached pH 6.5-7 and dried in oven at 105^{o}C for 12 hrs. Finally the activated carbon was sieved to 0.5mm particle size and sealed in polyethylene bag and stores for further characterization (El-Hendawy et al., 2001). Based on the literature review, the proportion of impregnating agent and raw material for this experiment selected 1:1 w/w and conducted as shown in the table 3-1 below (Mulugeta, 2014).

Table 3:1 Sample preparation using *Catha edulis* stems as a raw material to activated carbon

Sd.N	Temperature (^{0}C)	Activating Agent
1	500	H_3PO_4
2	500	H_2SO_4
3	500	KOH
4	550	H_3PO_4
5	550	H_2SO_4
6	550	KOH
7	600	H_3PO_4
8	600	H_2SO_4
9	600	KOH

***w/w – weight to weight ratio**

3.2.2. Characterization of the activated carbon

The produced activated carbon was determined by the proximate analysis. Bulk density was also determined in order to indirectly determine the porosity of the prepared activated carbon (Dada, et al., 2012), it was further characterized with FTIR (Fourier Transform Infrared Spectroscopy) and determination of pH value.

3.2.2.1. Bulk density

The bulk density was determined by taking the same particle size of 0.5mm by calculating the ratio of the mass to the volume occupied. A container of known volume of measuring cylinder was weighted without and with sample. The difference between the initial weight of the container and the final weight was calculated and mass difference was taken as the mass of the activated carbon. The bulk density was calculated from the relationship of mass to volume (Dada, et al., 2012; Omoniyi and Olorunnisola, 2014)

$$Bulk\ Density\ (\frac{kg}{m^3}) = \left[\frac{M}{V}\right] \quad (1)$$

Where, M= Mass of a sample (kg) and V= volume of the sample (m^3)

3.2.2.2. Proximate analysis

Proximate analysis includes moisture content (%) ASTM D2867, Volatile Matter Content (%) ASTM D5832, ash content (%) ASTM D2866. These were conducted in order to determine the fixed carbon content (%).

a. Moisture content

A gram of activated carbon weighed in a crucible weighing bottle and placed in a drying oven for 3 h at 150 ^{0}C. The sample then cooled in desiccators and weighed immediately to prevent moisture absorption.

$$Moisture\ Content\ (\%) = \left[\frac{W_1 - W_2}{W_1}\right] * 100 \quad (2)$$

Where:

W_1= weight of crucible with sample before drying (g)

W_2= weight of crucible with sample after drying (g)

b. Volatile matter content

A gram of activated carbon was weighed and placed in a dry and clean crucible (W_1) and inserted in a furnace at 900 °C for 7 min. The crucible was then cooled in a desiccator and weighed (W_2) and the volatile matter content was determined and expressed in percentage

$$Volatile\ matter\ content\ (\%) = \left[\frac{W_1 - W_2}{W_1}\right] * 100 \quad (3)$$

Where:

W_1 = weight of sample and crucible before heating (gram).

W_2 = weight of sample and crucible after heating (gram).

c. Ash content

Dried sample one gram was transferred into a predetermined crucible. The sample ignited until it was completely burned using muffle furnace at 650°C for 3h and then it was cooled in desiccators. The amount of ash was determined gravimetrically and expressed as percentage weight.

$$Ash\ content\ (\%) = \left[\frac{W_2}{W_1}\right] * 100 \quad (4)$$

Where:

W_1= weight of crucible with sample before heating (g)

W_2= weight of crucible with sample after heating (g)

d. Fixed carbon content

Fixed carbon content was determined by deduction of the moisture, volatile, and ash content % (Mulugeta, 2014; Omoniyi and Olorunnisola, 2014);

$$Fixed\ Carbon\ Content\ (\%) = 100 - (MC\% + VC\% + Ash\%) \quad (5)$$

Where,

MC% = Moisture content in percent

VC % = Volatile content in percent

Ash% = Ash content in percent

Minitab 17 was used in order to determine ANOVA for characterization and the P-value were determined. The ANOVA was determined for both bulk density and proximate analysis by using two factors (chemical and temperature) with its three levels. Hence by observing p value and its significance, the best AC for adsorption was selected.

3.2.2.3. Fourier transform infrared spectroscopy

The best activated carbon was further characterized for the functional group using FTIR. The FTIR analyses were conducted using spectrum 65 FT-IR (PerkinElmer) in a range from 4000 to 400cm^{-1} using KBr pellets at Addis Ababa University, chemistry department laboratory. FTIR spectrophotometry was used to determine the functional groups in both treated and untreated samples of activated carbon surfaces.

3.2.2.4. Determination of pH

The pH value was determined according to ASTM D1512 (ASTM 2010) by adding 1.0 g of AC in 100ml of distilled water in a 500mL beaker. Then the beaker was covered with watch glass and boiled on the hot plate for 5 min and set aside for a few moments to settle the bulk of AC particles. Poured off the supernatant liquid as soon as possible before it cools to 60 degree and pH value was measured by using pH meter (model 3305).

3.2.3. Experimental procedure for fluoride removal

The batch process adsorption was investigated using fluoridated 30mg/L water as an initial concentration. 30 mg/L was selected based on the average of Welenchiti wereda and Southern Afar (20-40 mg/L) of fluoride concentration. Alagumuthu et al., (2010a) studied the adsorption property of *Cynodon dactylon* activated carbon with varying range of dose from 0.25 g/L to 2.00 g/L. Form this study three doses of activated carbon 0.5g/L, 1.0g/L, and 1.5 g/L were selected. It was also observed the pH effect on the fluoride ion removal vary from 2 to 11. Good fluoride removal efficiency was determined at acidic condition and dropped at basic media (Suneetha et al., 2015). Therefore, acidic, neutral and basic pH media were selected to determine the good adsorption. Hence the levels were selected based on the above literature. The contact time (60, 90, 120 min) of activated carbon with the fluoride solution was selected based on the literature survey (Asheesh et al., 2012). The tests were conducted by applying three by three full factorial method with 3 times replication as shown in the table 3:2 below (Dosage of the adsorbent, pH level, and contact time).

Table 3:2 Factors and level for fluoride removal experiment

Factors	Minimum level	Intermediate level	Maximum level
Dosage (g/L)	0.5	1	1.5
pH	2	6.5	9
Contact time (min.)	60	90	120

The batch experiment was conducted using 250 ml flask by adding 100 ml of standard solution (30 mg/L) of fluoride concentration (C_i) in each run using magnetic stirrer at 120 rpm. The pH values were adjusted with 0.1N (HNO_3) and 0.1N (NaOH) (Rout et al., 2015). On selected each time the solution was allowed to settle for 2 minute and filtered using Whitman filter paper No 42 (Asheesh K. et al., 2012). The final aqueous solution (C_f) and TISAB (Baily, 1980) solution were placed in a beaker with equal volume ratio (1:1). TISAB is very important to regulate the ionic strength of samples and standard solutions. It also adjusts the pH and avoids interferences by polyvalent cations which are able to complex or precipitates with fluoride and reduce the free fluoride concentration in the solution. Fluoride ion selective electrode was immersed in a sample while stirring with magnetic stirrer. Then the reading was made after the value stabilizes (10-15min.). Hence

after settling it for 2 min. the smaller particle was removed by using filter paper. HNO_3 and NaOH were used for adjustment of pH solutions (Asheesh et al., 2012; Ramesh, 2012).

Table 3:3 Total runs of factors and their treatments

Run	Contact Time (min.)	pH factor	Dosage (g/L)
1	60	2	0.5
2	60	2	1
3	60	2	1.5
4	60	6.5	0.5
5	60	6.5	1
6	60	6.5	1.5
7	60	9	0.5
8	60	9	1
9	60	9	1.5
10	90	2	0.5
11	90	2	1
12	90	2	1.5
13	90	6.5	0.5
14	90	6.5	1
15	90	6.5	1.5
16	90	9	0.5
17	90	9	1
18	90	9	1.5
19	120	2	0.5
20	120	2	1
21	120	2	1.5
22	120	6.5	0.5
23	120	6.5	1
24	120	6.5	1.5
25	120	9	0.5
26	120	9	1
27	120	9	1.5

Blank solution was also conducted in order to see if the fluoride were adsorbed in the glass vessel. 40 ml of fluoride standard solution of 30 mg/L was added to 100 ml glass beaker and the same procedure was stirred on a magnetic stirrer at 120rpm. Then fluoride was determined every 1 hour. The results showed no significant change of concentration.

The experiment was carried out in full factorial of pH (2, 6 and 9), contact time (60, 90 and 120 min); and adsorbent load (0.5, 1.0 and 1.5 g/L) as shown in table 3-3 above and data analysis was carried out using Minitab 17 software. The statistical tool was used to

analyze the generated data (response). ANOVA was determined at a confidence level of 95%. The ANOVA P-Value of removal efficiency, main effect, and interaction effect were also determined and discussed in result section. The fluoride percentage uptake by the adsorbent (Sorption efficiency) and the amount of adsorbed fluoride were calculated using the following relationships. The fluoride concentration retained in the adsorbent phase, q_e (mg/g), was calculated (Bailey, 1980).

$$\text{Sorption efficiency (percent of Removal)} = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \quad (6)$$

$$\text{Amount adsorbed } (q_e) = \left[\frac{C_i - C_f}{M}\right] xV \quad (7)$$

Where,

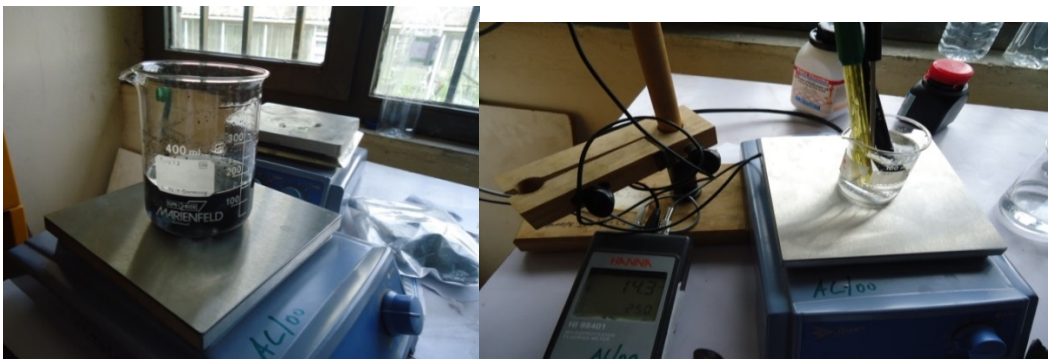
C_i = Initial concentration of fluoride in the solution (30mg/L)

C_f= Final concentration of fluoride ion in the solution (mg/L)

M= Mass of adsorbent (g/L)

V = Volume of solution (1lit)

q_e = Amount of fluoride ion adsorbed per gram of adsorbent (mg/g).



(a) (b)

Figure 3:1 Fluoride removal in aqueous solution

The above figures 3:1 (a) showed the fluoride removal in laboratory using magnetic stirrer and AC with fluoridated deionized water within the beaker. And (b) showed the portable fluoride meter.

3.2.4. Kinetics of adsorption

The adsorption kinetic was carried out in a time series (min.) for fixed amount of fluoride concentration (30 mg/L) of selected pH 2 and dose (1.5 g/L) at a room temperature stirring with magnetic stirrer at 120 rpm. These factors were chosen as the best fluoride removal efficiency result from the batch adsorption. The equilibrium reached when the adsorbent can no longer adsorbs the adsorbate (Bansal and Goyal, 2005). The kinetic analysis of the adsorption data was investigated by using reaction kinetics of pseudo - first - order and pseudo - second - order mechanisms.

Pseudo-first-order adsorption:

$$-\left[\frac{dq_t}{d_t}\right] = k_1\left(q_e - q_t\right) \quad (8)$$

By rearranging, integrating both sides and by applying the boundary condition t=0 to t_f and q_t=0 to q_e then the equation will be (Ho and McKay, 1998b);

$$log\left(q_e - q_t\right) = log(q_e) - \frac{k_1}{2.303}t \quad (9)$$

Where, q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively.

k_1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model.

The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t becomes linear from which k_1 and q_e determined as the slop and intercept of the plot, respectively. Hence in this equation can be expressed as a linear form; Y=m X + b, where Y axis is log ($q_e - q_t$); log (q_e) is intercept b; and $\frac{k_1}{2.303}$ is the slope m. The application of the pseudo-first order equation to experimental data differs due to the parameter k_1 (q_e-q_t) which does not represent the number of available sites and the parameter log (q_e) is an adjustable parameter and often not found equal to the intercept of the plot log ($q_e - q_t$) versus t. But in true first order, log (q_e) should be equal to the intercept of log (q_e-q_t) versus t (Ho and McKay, 1998b).

Pseudo-second-order adsorption:

$$-\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (10)$$

Where, k_2 (min^{-1}) is the pseudo-second-order rate constant for the kinetic model (HO and McKay, 1998 (a); Ho, 2006). Then by integrating and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_e then the result will become;

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (11)$$

Then by rearranging the equation (11) to a linear form;

$$\left[\frac{t}{q_t}\right] = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (12)$$

The plot of (t/q_t) and t of equation (12) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Therefore for both pseudo first – order - kinetics and pseudo second – order kinetics the experimental data were plotted in a graph, and then from the curves the parameters for both kinetic models were calculated. The correlation coefficient for pseudo second order kinetics is compared with correlation coefficient of pseudo first order kinetics and the best model that fits the experimental data is selected.

Lagergren's (1898) model is widely applied to data modeling. This equation has been used to study the rate constant for adsorption. It describes the solute uptake rate which in turn governs the residence time sorption reaction. The adsorption kinetics is an important factor in determining the effectiveness of an adsorbent in removal of fluoride (Sharma, 2012).

3.2.5. Adsorption isotherms

Adsorption isotherm was carried out by applying series of dosage at a 2 pH, time 60min. and 30 mg/L of initial fluoride concentration. The constant factors were selected from the best result of fluoride removal efficiency. The amount of solute adsorbed per adsorbent (q_e) (mg/g) as a function of the equilibrium concentration of the solute in the bulk solution (C_e), at a constant temperature, is called the adsorption isotherm. Adsorption isotherm mostly investigated by using two common isotherm models, Freundlich and Langmuir isotherm models (Sharma, 2012).

$$q = f(C_e) \quad (13)$$

Freundlich isotherm is an empirical expression in;

$$q = K\, C_e^{1/n} \quad (14)$$

Where,

q = amount of solute adsorbed per unit weight of adsorbent = x/m (mg/g)

C_e = equilibrium concentration of the solute (g/m^3)

K, 1/n = isotherm constants

K_f is the measure of adsorption capacity and 1/n is the measure of adsorption intensity.

On linearization, the equation takes the form;

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (15)$$

K_f and 1/n are the constants, which represent adsorption capacity and adsorption intensity respectively. The values of K_f and n were obtained from the slope and intercept of the plot between log (q) and log C_e. Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces and is the earliest known relationship describing the adsorption equilibrium (Alagumuthu et al, 2010a).

Langmuir isotherm is represented by;

$$q = \frac{bq_m C_e}{1 + bC_e} \quad (16)$$

Where,

q_m = maximum adsorption capacity (mg/g)

b = Langmuir isotherm constant

On linearization, the equation takes the form;

$$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{bq_m}\right)\left(\frac{1}{C_e}\right) \quad (17)$$

The Langmuir isotherm was based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no transmigration of adsorbate in the plane of the surface Langmuir isotherm sorption takes place at specific homogeneous sites within the adsorbent (Sharma, 2012).

3.2.6. Fixed bed adsorption process

Continuous flow laboratory column was developed to see the result of defluoridation. The procedure was conducted using maximum efficiency from batch studies. It was made

from glass column tube with 10 mm diameter (Iman et al., 2013) containing 1.5 g of activated carbon and flow of 30 mg/L standard fluoride solution (pH 2) at rate of 2ml/min. Cotton pad and stop cock was used so that the activated carbon particle not to leave the column. Plastic bottle was used as reservoir of the fluoride solution (Ahmedin, 2007). Then the sample was taken at 30 min. interval on the other end to determine the residual fluoride concentration so that fluoride removal efficiency determined.

4. RESULTS AND DISCUSSION

4.1.Characterization of activated carbon

4.1.1. Bulk density

The bulk density (kg/m^3) was conducted for every treated activated carbon from H_3PO_4, H_2SO_4, and KOH at different temperature (500°C, 550°C, and 600°C) at constant particle size of around 0.5mm. The result obtained is shown in table below and the detail calculation is also included under (Appendix A-1).The average results are shown in fig.4:1 below.

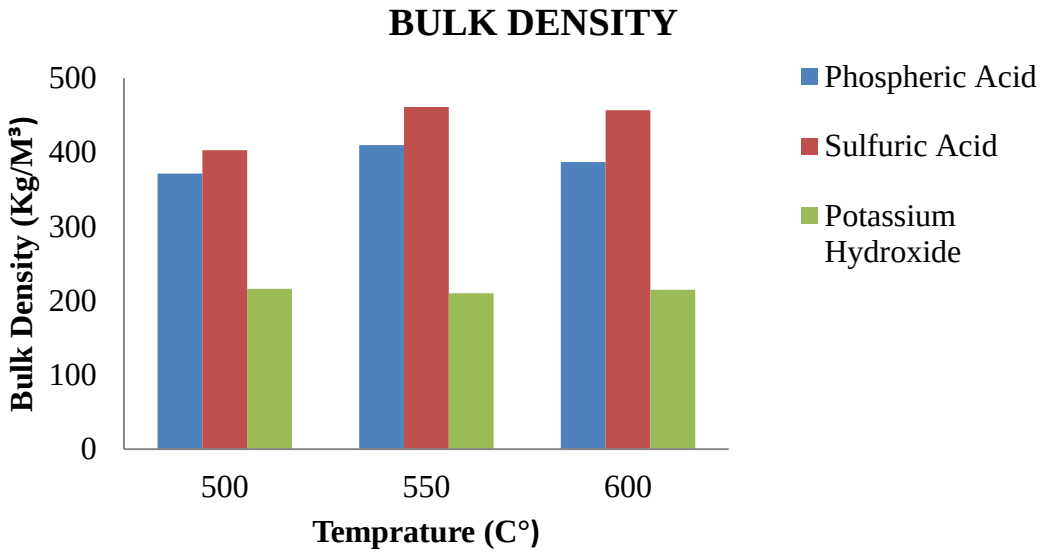


Figure 4:1 Bulk density for activated carbon with respect to different temperature applications and chemical treatments.

The above chart fig. 4:1 shows the result of bulk density comparing of the activated carbon products which were treated subsequently with chemical impregnated agent and physical (temperature) activation method. There is a difference of bulk density of the activated carbon treated with acids and base. The samples treated with KOH showed a very low density comparing to H_3PO_4 and H_2SO_4. ANOVA analysis of bulk density showed that the effect between chemicals (H_3PO_4, H_2SO_4, and KOH) and temperature (500°C, 550°C, and 600°C) are (P=0.000) indicating a highly significant value at the table below. For further details, see Appendix B-5. Except with interaction between H_3PO_4 and 500°C (P=0.646), which indicate highly insignificant. And the sample treated with H_2SO_4

showed a very high bulk density from the rest of the activated carbon in each temperature. The bulk density of the activated carbon product treated with phosphoric acid and sulfuric acid, increased with the increase of temperature from 500°C to 550°C then almost became constant at 600°C. While potassium hydroxide treated biomass of the activated carbon showed a different result concerning pyrolyzation at different temperature. The average results obtained that as the temperature increased from 500°C to 550°C the bulk density decreased then slightly increased at 600◦C. Even though the bulk density seem to decrease when temperature increases, the statistical analysis indicates insignificant difference between 550°C to 600°C (P=0.000) with significant value. The table below shows the p-values evaluated from ANOVA on bulk density.

Table 4:1 ANOVA for bulk density.

Chemicals*Temperature	Coefficient	P-Values
H2So4 500	-19.638	0.0000
H2So4 550	8.37	0.0000
H2So4 600	11.269	0.0000
H3Po4 500	-0.366	0.6460
H3Po4 550	7.782	0.0000
H3Po4 600	-7.416	0.0000
KOH 500	20.004	0.0000
KOH 550	-16.151	0.0000
KOH 600	-3.8530	0.0000

The increase in bulk density at higher temperature is due to the collapse of the carbon structure or the activation process which might stabilize thermally resulting in pore size reduction of the activated carbon (Yang et al, 2011). A similar effect was observed in activating pumpkin seed shell at 600°C which degraded the surface area and porosity of the produced activated carbon (İlknur and Canan, 2016). In sulfuric acid treatment, the carbon structure affected during activation to unfavorable condition of porosity. A similar situation was reported when acid pretreated biomass activated at high temperature, the porous structures and developed walls in the chars were damaged, hence it become so thin and collapses causing a reduction on the surface area (Espantaleon et al., 2003; Gürses et al., 2004; Wang et al., 2004; Alkan et al., 2005; Annadurai et al., 2007; Ofomaja, 2007; Noroozi et al., 2007). This was perhaps that the acids reacted with the carbon – oxygen bond of the lignocellulosic material and degraded the bond structure and also resulting in condensation of the extractive substances in the biomass and lower pore volume.

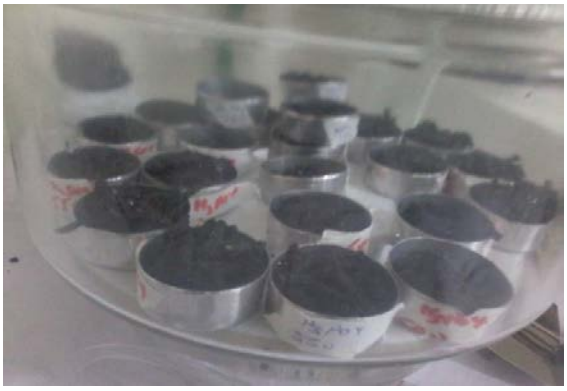
However, the result obtained using KOH, the temperature has actively enhanced the KOH action and the carbon structure started to expand forming a larger volume and surface areas, as a result the bulk density of the activated carbon become lower than the other treatment methods. The reaction took place when thermal pyrolysis was applied to KOH activated biomass carbon, the carbon bond structures started to change by expanding in to a bloating manner. KOH acted very differently with carbon skeleton and gave rise to porosity which leads to good adsorption capacity property. A higher volume of activated carbon will deliver a greater surface area for adsorption of micro-pollutants and it is known that the lower the bulk density the higher porosity (Menendez-Diaz and Martin-Gullon, 2006).

(a)

(b)

(c)

(d)



(e) (f)

Figure 4:2 Production process of activated carbon (a) chopped of raw material for impregnation (b) impregnated sample with chemicals, (c) sample after impregnation and dried, (d-e) activated carbon at different temperature, (f) activated carbon and ready for adsorption process.

The bulk density of AC, produced with H_3PO_4 and H_2SO_4 treatment of the biomass, increased with temperature increase from 500°C to 550°C (372 to 410 kg/m^3) and (400 to 461 kg/m^3) respectively, while the base catalyzed activated carbon at temperature of 500°C, 550°C and 600°C was 216, 210, and 215 kg/m^3 respectively.

4.1.2. Proximate analysis

After activation process the activated carbon was analyzed for the moisture content (%) ASTM D2867, Volatile Matter Content (%) ASTM D5832, and ash content (%) ASTM D2866. The detail calculations are included under (Appendix-A-2, 3, 4). The results in table 4:2 show that the AC produced from sulfuric acid treatment have the highest ash content (18%, 18%, and 20%) as the temperature increased from 500°C, 550°C and 600°C than the rest of the produced AC. The statistical analysis for ash content in an interaction between sulfuric acid AC and temperature also seemed to show (p=0.06) at a temperature 500°C, and for 600°C (p=0.324) which indicates insignificant value, however there was significant value (p=0.007) for 550°C temperature. The ash content shown in table 4:3, the interaction of phosphoric acid and temperatures showed a highly insignificant value (p=0.782, 0.754, and 0.557). And for KOH interaction with temperature (500°C and 550°C) showed significant, while for 600°C (p=0.683) indicating an insignificant. For full details see (Appendix B-4). Generally the ash content of produced activated carbon significantly differ between and within each other.

Table 4:2 Proximate analysis for the treateds amples

Samples	Moisture Content	Volatile Content	Ash Content	Fixed Carbon
H_3PO_4, 500°C	10%	35%	7%	48%
H_3PO_4, 550°C	7%	28%	8%	58%
H_3PO_4, 600°C	9%	27%	8%	56%
H_2SO_4, 500°C	8%	31%	18%	43%
H_2SO_4, 550°C	4%	26%	18%	53%
H_2SO_4, 600°C	6%	24%	20%	50%
KOH, 500°C	9%	27%	5%	60%
KOH, 550°C	4%	20%	7%	69%
KOH, 600°C	3%	21%	7%	69%

Table 4:3 ANOVA for ash content

Chemicals*Temperature	Coefficient	P-Values
H2So4 500	0.00607	0.06
H2So4 550	-0.00915	0.007
H2So4 600	0.00307	0.324
H3Po4 500	0.00085	0.782
H3Po4 550	0.00096	0.754
H3Po4 600	-0.00181	0.557
KOH 500	-0.00693	0.035
KOH 550	0.00819	0.015
KOH 600	-0.00126	0.683

The volatile matter activated carbon produced from treatment of sulfuric and phosphoric acid higher than the AC produced with the treatment of potassium hydroxide (Appendix A-4). Observing the P-value of volatile content sulfuric acid treated samples of activated carbon shows highly insignificant of (p=0.659) at 500°C, at 550°C (p=0.176), and 600°C (p=0.349). The highest insignificant of phosphoric acid treated sample was obtained at 550°C (p= 0.730). The least insignificant value were obtained at KOH (p=0.303 and

0.106) at 500°C and 600°C due to the low percentage of volatile content. For more details, see (Appendix B-3).

Table 4:4 ANOVA for volatile content.

Chemicals*Temperature	Coefficients	P-Values
H2So4 500	-0.00204	0.659
H2So4 550	0.00641	0.176
H2So4 600	-0.00437	0.349
H3Po4 500	0.00496	0.289
H3Po4 550	-0.00159	0.73
H3Po4 600	-0.00337	0.468
KOH 500	-0.00293	0.528
KOH 550	-0.00481	0.303
KOH 600	0.00774	0.106

The fixed carbon content in the produced activated carbon varied from 47 % to 69 % depending on the interaction of processing factors, there was a significant difference among the interactions. The fixed carbon in the activated carbon produce with the treatment of KOH at different temperature showed insignificant, and 550°C lowest value among the AC. For further details see (Appendix B-1).

Table 4:5 ANOVA for fixed carbon.

Chemicals*Temperature	Coefficients	P-Values
H2So4 500	0.00084	0.915
H2So4 550	0.00428	0.589
H2So4 600	-0.00512	0.518
H3Po4 500	-0.0014	0.859
H3Po4 550	0.00249	0.752
H3Po4 600	-0.0011	0.89
KOH 500	0.00056	0.944
KOH 550	-0.00677	0.395
KOH 600	0.00622	0.434

High amount of moisture and volatile content also has been reported (Ahmad et al, 2015). Hence, when the temperature of activation increases, the volatile percentage decreases. Hence this could mean that higher temperature treatments of the carbon material by removing gaseous compounds, favors increasing fixed carbon chars, forming pore structure and increase surface areas. Same goes with moisture content, high amount of

temperature seemed to take all of the moisture leaving carbon structure and tars (Smíšek and Černý, 1970).

Table 4:6 ANOVA for moisture content

Chemicals*Temperature	Coefficient	P-Values
H2So4 500	-0.00488	0.527
H2So4 550	-0.00154	0.841
H2So4 600	0.00642	0.407
H3Po4 500	-0.00442	0.567
H3Po4 550	-0.00186	0.808
H3Po4 600	0.00628	0.417
KOH 500	0.0093	0.235
KOH 550	0.0034	0.658
KOH 600	-0.0127	0.11

High percentage of ash content was reported from pine bark (16.12%) (Mohan 2012) and rice husk (20.6%) (Anchan and Kunio, 2012) which were similar or even higher than that of sulfuric acid treated carbon produced from *Catha edulis*. The high content of ash can be explained from that of the raw material behavior (table 4.2) however the high ash content in *Catha edulis* activated carbon could be explained from the treatment process which the sulfuric acid treated product may not be washed with HCl as proposed. High amount of ash content is not favorable for AC to be a good adsorbent which result in low carbon content which in turn can lower the adsorption capacity and efficiency. Hence the lower the ash content, the better the adsorbent (Tsai et al, 2009; Mohan et al., 2012; Anchan and Kunio, 2012).

The selection of parameter based on the significance value in proximate analysis and bulk density, therefore, the production of the activated carbon for adsorption study done with KOH at 550 °C. The table 4-2 shows the comparison of produced treated and untreated activated carbon. This shows that the KOH treated material contains larger volume hence indicates as a good adsorbent and the adsorption efficiency would be higher. The ash content of activated carbon produced from *Catha edulis* pretreated with potassium hydroxide shows lower ash content compared to other treated carbon. As mentioned earlier, the activated carbon with pretreatment of KOH had statistically a significant difference from other treatments.

Table 4:7 Treated and untreated carbon,

Parameters	Untreated, 550 °C	KOH Treated, 550 °C
Moisture Content	2%	4%
Volatile Content	21%	20%
Ash Content	14%	7%
Fixed Carbon	63%	69%
Bulk Density(Kg/m^3)	350.72	210
pH Value	10.7	6.7
Yield of Raw Material %	20%	22%
Ca %	2.5	-
Mg %	0.761	-
Na %	0.0756	-
K %	1.313	-

The moisture and ash content of the KOH treated AC was found very close to other research reports on pumpkin (İlknur and Canan, 2016), pine wood (Mohan et al., 2012), corn stover (Mohan et al., 2012), soybean (Tay et al, 2009), *Acacia nilotica* stalk (Shivayogimath et al 2014). However, the bulk density of the treated AC shows less than the commercial available AC (Anonymous 2012), hence this is result is due to the KOH effect on the raw material. Studies indicated that the lower the bulk density the higher the porosity (Ademeso et al., 2012), therefore, the activated carbon produced with KOH treatment at 550°C was selected as an adsorbent, high in volume and fixed carbon. The temperature effect was significant (p=0.000), so the activated carbon produced with potassium hydroxide treatment of the studied biomass at 550°C with high fixed carbon (69%) which could be used in adsorption of fluoride from aqueous solution.

4.1.3. FTIR analysis result

The graph shown figure 4-3 below indicated for both treated and untreated activated carbon shared similar threads. However observing the untreated carbon shows that higher stretches than treated one. In an untreated sample the around 3300-3600 cm^{-1} indicates the presence of O-H effect of acid, alcohol, or phenols functional group. And around 1500-1600 cm^{-1}, is CO_2 stretching from carboxylate bond. The around 1425 cm^{-1} is due to the C-C stretching of the aromatic structure; and around ~800 indicates C=CH stretching structure (Dudley and Fleming, 1995). Observing the untreated carbon, it seemed to have high amunt of OH group than the treated one. So when KOH was used as chemical agent for activation, the OH bonds were reduced and mostly the carbon remained.

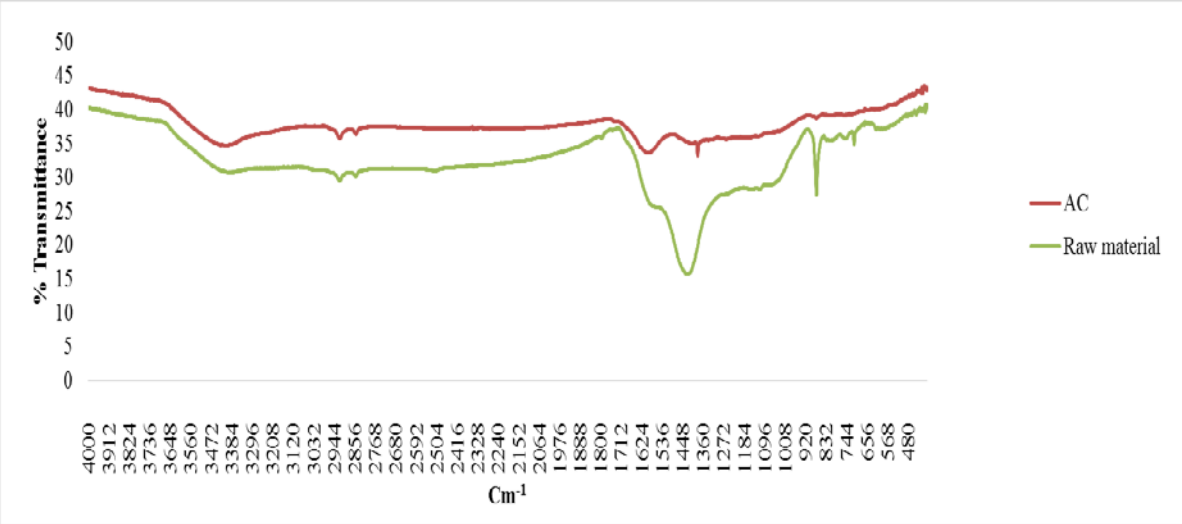


Figure 4:3 FTIR spectrophotometry results for treated and untreated activated carbon adsorption of fluoride ion

4.2. Adsorption of fluoride ion

Based on the above studies on the production and characterization of the activated carbon from *Catha edulis*, KOH as chemical impregnator and temperature of 550 °C were selected. The activated carbon from *Catha edulis* produced at 550 °C with KOH activating agent, the adsorption of fluoride was measured and the result indicates that an increase of dose showed a significant variation in adsorption of fluoride ion.

4.2.1. Main effects and interaction effects

The factors and their interaction were compared at p=0.05 and the R square indicates that is close to 1 (0.98) found in (Appendix B-6).

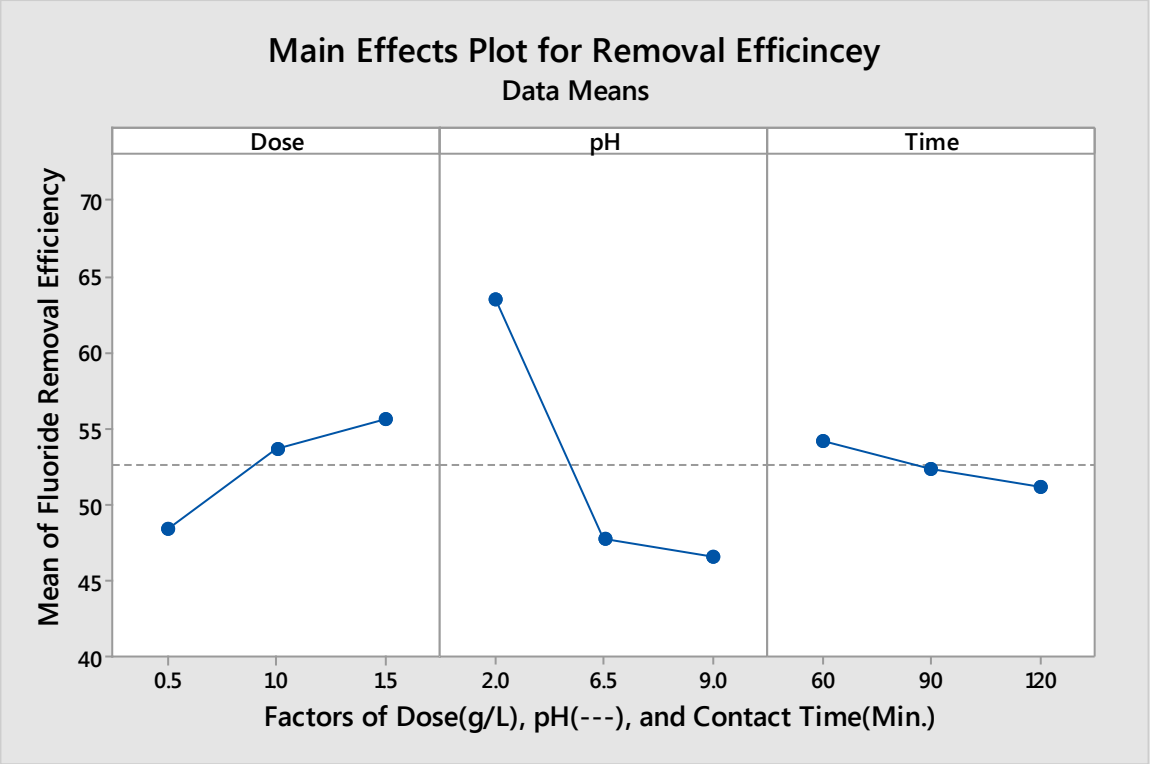


Figure 4:4 Main effects mean floride adsorption

Residual plots for fluoride removal efficiency were also shown under (Appendix B-6) and have four graphs.

Table 4:8 ANOVA on main effects

Term Constant	Coefficients	P-Value
Dose		
0.5	-4.227	0.000
1	1.119	0.000
1.5	3.109	0.000
pH		
2	10.899	0.000
6.5	-4.881	0.000
9	-6.017	0.000
Time		
60	1.563	0.000
90	-0.175	0.435
120	-1.388	0.000

ANOVA indicated that the main effect especially dose and pH shows highly significant. The main effect of time however showed insignificant value (0.435) at 90 min. The main effect plot of pH factor fig. above showed the strongest effect in fluoride removal efficiency. The table above showed the p-value of each main effect.

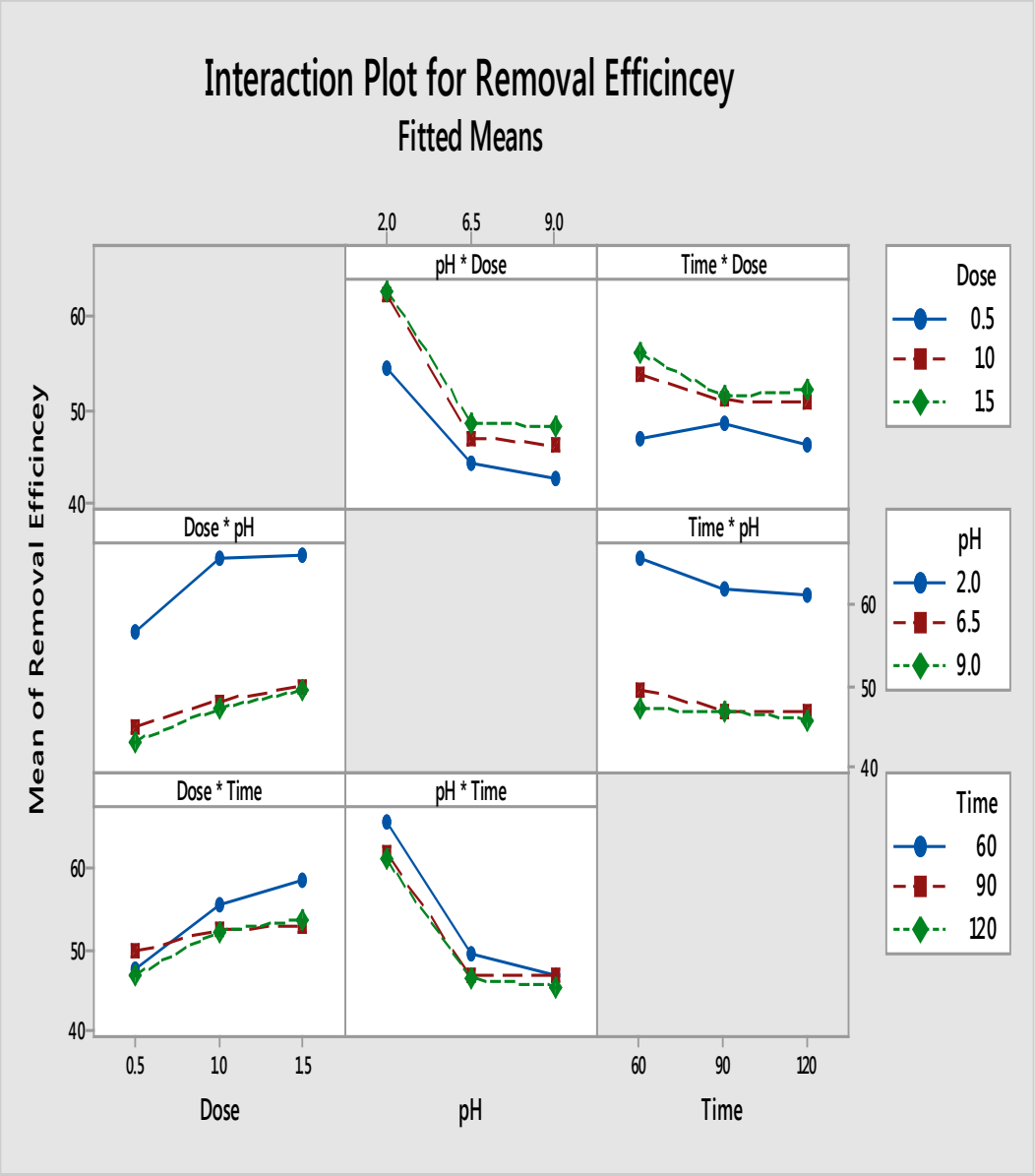


Figure 4:5 Effect of factors interaction versus removal efficiency of fluoride

The fig. 4:5 showed the interaction effects plot for removal efficiency using two factors interaction (two-way interactions). The overall interaction effects show both significant and insignificant p-values Looking at the details, dose*pH with respect to levels, the p-values have at 1.0 g/L dose *9 pH (p=0.127), and 1.5 g/L dose and 9 pH (p=0.229), which are insignificant values. Then by looking at the rest of the two-way interaction

(Dose*Time, and pH*Time), most of the p-values depending on the levels, have high insignificant values. This indicates that when time has less significant effect when it interacts with the other levels as shown in the table below. For further detail see (Appendix B-6).

Table 4:9 ANOVA in two-way interaction effects

Term Constant	Coefficients	P-Value
Dose*pH		
0.5 2.0	-2.356	0.000
0.5 6.5	1.536	0.000
0.5 9.0	0.82	0.012
1.0 2.0	1.225	0.000
1.0 6.5	-0.736	0.023
1.0 9.0	-0.489	0.127
1.5 2.0	1.131	0.001
1.5 6.5	-0.8	0.014
1.5 9.0	-0.331	0.299
Dose*Time		
0.5 60	-1.946	0.000
0.5 90	1.793	0.000
0.5 120	0.153	0.629
1.0 60	0.635	0.049
1.0 90	-0.812	0.013
1.0 120	0.178	0.575
1.5 60	1.311	0.000
1.5 90	-0.98	0.003
1.5 120	-0.331	0.299
pH*Time		
2.0 60	0.743	0.022
2.0 90	0.119	0.709
2.0 120	-0.862	0.008
6.5 60	0.338	0.288
6.5 90	-0.627	0.052
6.5 120	0.289	0.364
9.0 60	-1.081	0.001
9.0 90	0.509	0.113
9.0 120	0.573	0.075

4.2.2. Combined effect

4.2.2.1. Effect of pH value

One of the important factors for fluoride adsorption is pH within solution and affects the removal efficiency. The effect of pH on fluoride removal of the activated carbon from *Catha edulis* were conducted at pH of 2, 6.5, and 9. The average fluoride removal efficiency results are shown in the figures below.

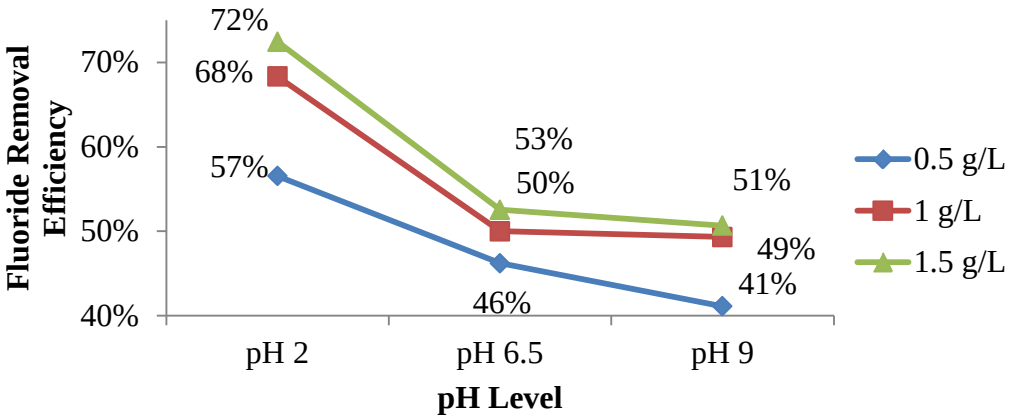


Figure 4:6 Effect pH at 60 min. time

As shown in fig 4:6, the average fluoride adsorption efficiency varied depending on the pH value and dose. In this experiment, observed that for all pH levels as the adsorbent dose increased, the removal efficiency of the activated carbon increases. The removal efficiency of the activated carbon in acidic media is much more effective than in neutral and basic media. Among the three pH levels, pH 2 can adsorb up to the average of 57%, 68%, and 72% efficiency for doses of 0.5, 1.0, and 1.5 g/L respectively. The adsorption efficiency in acidic medium is statically significant at p=0.015 level using 1.5 g/L dose. Better adsorption efficiency with activated carbon were reported from acidic medium (Tembhurkar and Dongre 2006; Suneetha et al 2015). Adsorption in neutral solution, the load ratio at 1.0 g/L and 1.5 g/L showed insignificant difference except for 0.5 g/L, which showed significant difference (p=0.006) and in basic medium the adsorption more affected with a significant level of p=0.024 at dose of 1.0 g/L.

Table 4:10 ANOVA of pH effects at constant contact time 60 min.

Time*Dose*pH	Coefficients	P-Value
60 0.5 2.0	-0.694	0.126
60 0.5 6.5	1.267	0.006
60 0.5 9.0	-0.573	0.204
60 1.0 2.0	-0.422	0.348
60 1.0 6.5	-0.61	0.177
60 1.0 9.0	1.032	0.024
60 1.5 2.0	1.116	0.015
60 1.5 6.5	-0.657	0.147
60 1.5 9.0	-0.459	0.308

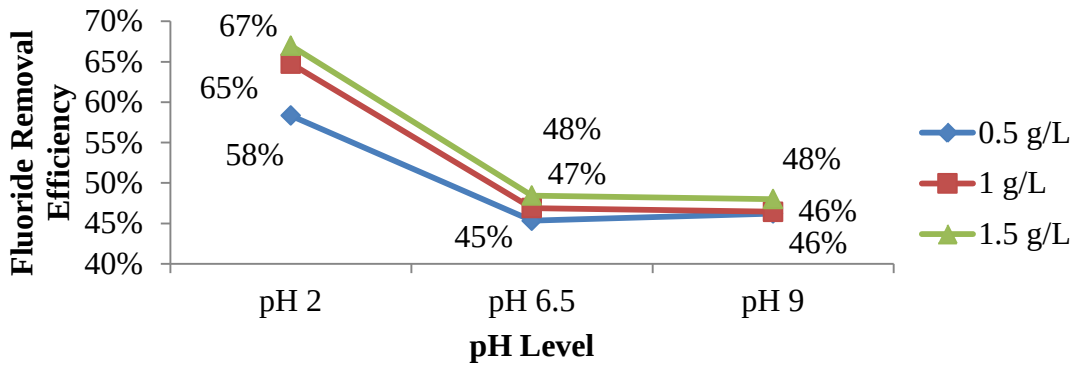


Figure 4:7 Effect pH at 90 min. time

The fig 4:7 above showed higher removal efficiency of fluoride at pH 2 (67%, 65%, and 58%) for respective activated carbon dose of 0.5, 1.0 and 1.5 g/L with contact time of 90 minutes. The efficiency of AC dropped as the pH changed from acidic to neutral and basic. The neutral and basic media showed insignificant values. However the change in adsorption efficiency significantly differ (p=0.038) at basic medium and 0.5 g/L dose has lower adsorption than the other doses. This indicates that the removal of fluoride mainly depends of the pH value where the surface of AC more protonated and able to attract the fluoride ion from the solution. When the pH increased from acidic 2.0 to 6.5, the removal efficiency started to drop to (67%, 65%, and 58%) and (48%, 46%, and 46%) for each dose of 0.5, 1.0 and 1.5 g/L respectively.

Table 4:11 ANOVA of pH effects at constant contact time 90min.

Time*Dose*pH	Coefficients	P-Value
90 0.5 2.0	-0.291	0.516
90 0.5 6.5	-0.657	0.147
90 0.5 9.0	0.948	0.038
90 1.0 2.0	-0.168	0.708
90 1.0 6.5	0.43	0.340
90 1.0 9.0	-0.262	0.560
90 1.5 2.0	0.459	0.308
90 1.5 6.5	0.227	0.613
90 1.5 9.0	-0.686	0.130

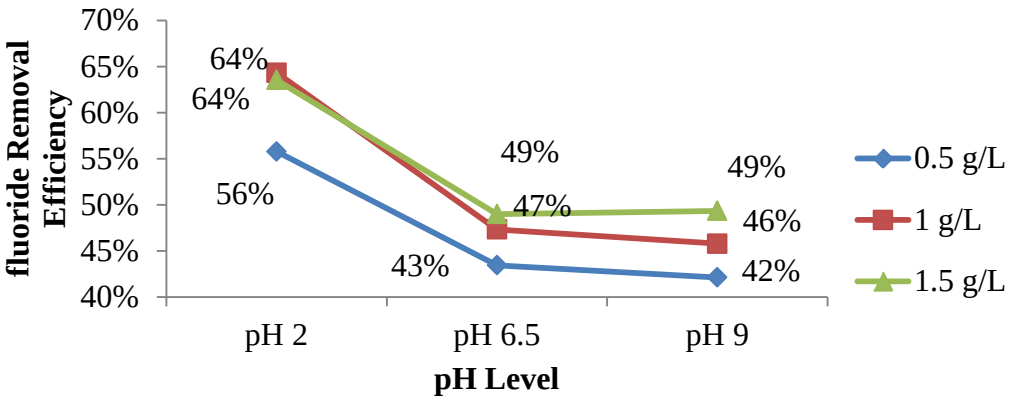


Figure 4:8 Effect pH at 120 min. time.

As in fig. 4:8 shown above, the fluoride removal efficiency is higher at pH 2 (64, 64 and 56%) than at pH 6.5 (49, 47 and 43%) and at pH 9 (49, 46 and 42%) with the corresponding load ratios of 0.5, 1.0 and 1.5 g/L. From the result observed high fluoride adsorption at high adsorbent load of 1.5 g/L in statistically differing (p=0.001) level than at 0.5 g/L (p=0.031) doses in acidic medium. Also the statistical analysis obtained that at dose of 1.5 g/L, the adsorption efficiency significantly changed from acidic to neutral media (P=0.001 to 0.340) from 64% to 49% at a contact time of 120 min. The result indicates that higher removal efficiency of fluoride of 72.4% was observed at a loading of 1.5 g/L AC of pH 2 solution within 60 min. Then as the pH increased to neutral and basic medium the removal efficiency drops instantly. One of the possible reasons is that the cationic groups might compete to bind on the adsorbent surface instead of fluoride ions which indicates that the wide application of activated carbon in the removal of anion or cation.

Table 4:12 ANOVA of pH effects at constant contact time 120min.

Time*Dose*pH	Coefficients	P-Value
120 0.5 2.0	0.985	0.031
120 0.5 6.5	-0.61	0.177
120 0.5 9.0	-0.375	0.404
120 1.0 2.0	0.59	0.191
120 1.0 6.5	0.18	0.688
120 1.0 9.0	-0.77	0.090
120 1.5 2.0	-1.575	0.001
120 1.5 6.5	0.43	0.340
120 1.5 9.0	1.146	0.013

Hence when the solution media becomes basic, both OH^- and F^- ions start to compete as they have similar charges (Jamode et al.,2013) and could deprotonate the active sites at the surface of the adsorbent which causes reduction of fluoride adsorption (Kumar et al., 2008; Habuda-Stanić et al.,2014). The adsorption efficiency of activated carbon depends on the dose of adsorbent, as a result the removal percentage in different pH showed variation.

4.2.2.2. Effect of contact time

Effects of contact time on adsorption of the fluoride ion in batch process were studied and the results are shown in a figure below.

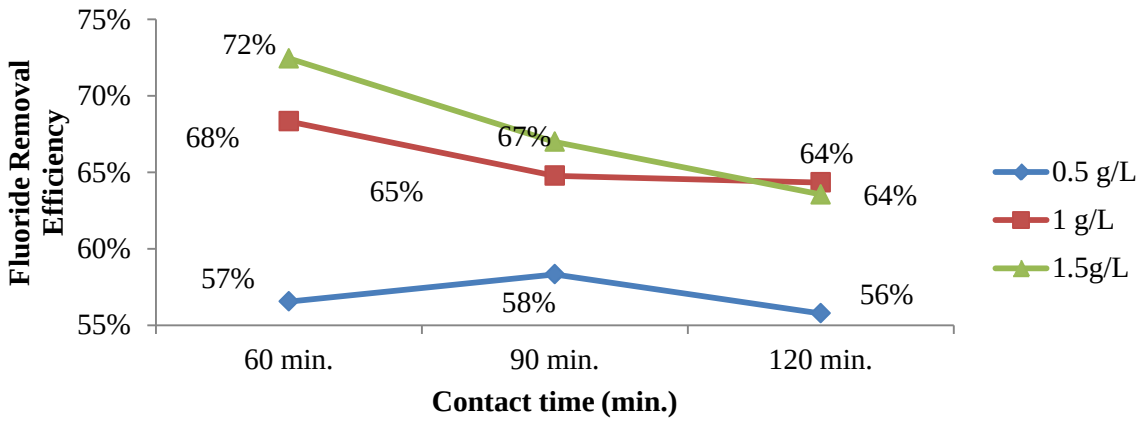


Figure 4:9 Effect contact time on adsorption effecieny at constant at pH 2.

The figure 4:9 showed that at pH 2 with contact time for 60, 90, and 120 min at different dose of 0.5, 1.0, and 1.5 g/L, of the fluoride removal efficiency. In each contact time, the removal efficiency varies due to the amount of dose applied. The highest removal efficiency (72%) was observed at 1.5 g/L of dose with a contact time of 60 min, then

significantly changed at 90 min (67%) (P=0.308), in which has a insignificant value. At dose 0.5 g/L the adsorption efficiency dropped from 58% to 56% with significantly (p=0.516 to 0.031). And at dose 1 g/L, the adsorption of fluoride efficiency decreased insignificantly as time increased from 60 min (68%), 90min (65%), and 120 min (64%) at p-value (0.348, 0.708, and 0.191) where similar effect was observed when using activated bagasse carbon to remove fluoride from aqueous solution as the contact time increased from 60 to 75 min, the removal efficiency slightly decreased (Asheesh et al, 2012).

Table 4:13 ANOVA of contact time effects at constant pH 2

pH*Dose*Time	Coefficients	P-Value
2.0 0.5 60	-0.694	0.126
2.0 0.5 90	-0.291	0.516
2.0 0.5 120	0.985	0.031
2.0 1.0 60	-0.422	0.348
2.0 1.0 90	-0.168	0.708
2.0 1.0 120	0.59	0.191
2.0 1.5 60	1.116	0.015
2.0 1.5 90	0.459	0.308
2.0 1.5 120	-1.575	0.001

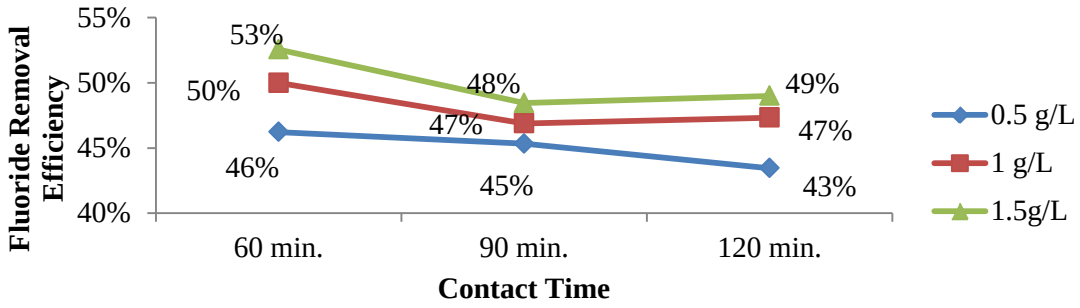


Figure 4:10 Effect contact time on adsorption effecieny at constant pH 6.5.

As the figure 4:10 shows, similar to the acidic media, the higher removal efficiency was obtained at contact time of 60 min in every dosage used. Then it started to insignificantly drop when the contact time increased to 90 and 120 minutes. At dose 0.5 g/L, the contact time (60min.) was obtained at 46% removal efficiency at P=0.006 which indicated the significant difference with the increase of contact time to 90min. But further increase in contact time to 120min, the removal efficiency started to insignificantly differ (p=0.177)

decreasing to 43%. When using 1 g/L and 1.5 g/L dose, the removal efficiency showed insignificant effect as the contact time increased.

Table 4:14 ANOVA of contact time effects at constant pH 6.5

pH*Dose*Time	Coefficients	P-Value
6.5 0.5 60	1.267	0.006
6.5 0.5 90	-0.657	0.147
6.5 0.5 120	-0.61	0.177
6.5 1.0 60	-0.61	0.177
6.5 1.0 90	0.43	0.340
6.5 1.0 120	0.18	0.688
6.5 1.5 60	-0.657	0.147
6.5 1.5 90	0.227	0.613
6.5 1.5 120	0.43	0.340

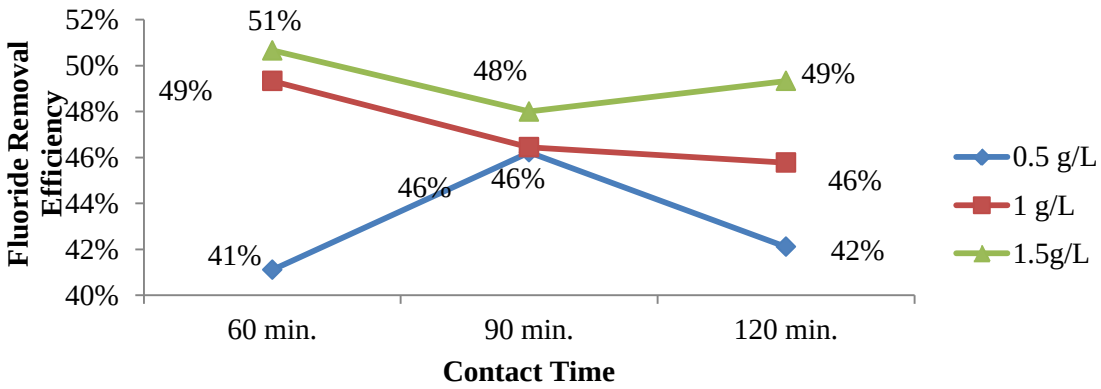


Figure 4:11 Effect contact time on adsorption effecieny at constant at pH 9.

Fig 4:11 shows the removal efficiency of fluoride in varying time, that the adsorption efficiency of the AC at dose 0.5 g/L showed a significant difference at 60 min. to 90 min. (0.204 to 0.038), but at contact time 120min. P-value (0.404) indicating insignificant value. When a dose of 1 g/L was used, the removal efficiency at 60min was resulted 49% removal of fluoride which is significantly differing (p=0.024) from contact time of 90min and 120min. When a dose of 1.5 g/L was used, the removal efficiency decreased insignificantly (P=0.308 to 0.130) from 51% at 60th min. to 48% at 90th min. Then at 120min., the removal efficiency (49%) show a significant change (p=0.013).

Table 4:15 ANOVA of contact time effects at constant pH 9

pH*Dose*Time	Coefficients	P-Value
9.0 0.5 60	-0.573	0.204
9.0 0.5 90	0.948	0.038
9.0 0.5 120	-0.375	0.404
9.0 1.0 60	1.032	0.024
9.0 1.0 90	-0.262	0.560
9.0 1.0 120	-0.77	0.090
9.0 1.5 60	-0.459	0.308
9.0 1.5 90	-0.686	0.130
9.0 1.5 120	1.146	0.013

4.2.2.3. Effect of adsorbent dosage

The effects of adsorbent dosage at different contact time and pH value on fluoride adsorption experiment were conducted and the results of fluoride removal presented and discussed below.

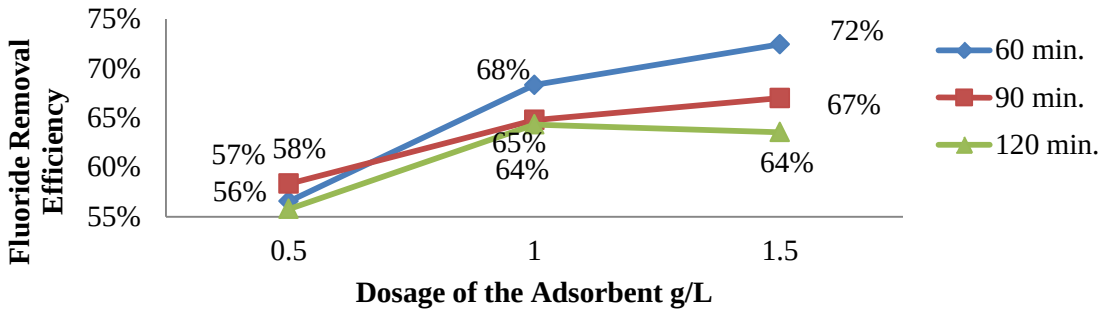


Figure 4:12 Effect dose on adsorption efficiency at pH 2.

Figure 4:12 illustrates that increasing dose of the adsorbent, the removal efficiency increases.

Table 4:16 ANOVA of dose effects at constant pH 2

pH*Dose*Time	Coefficients	P-Value
2.0 0.5 60	-0.694	0.126
2.0 0.5 90	-0.291	0.516
2.0 0.5 120	0.985	0.031
2.0 1.0 60	-0.422	0.348
2.0 1.0 90	-0.168	0.708
2.0 1.0 120	0.59	0.191
2.0 1.5 60	1.116	0.015
2.0 1.5 90	0.459	0.308
2.0 1.5 120	-1.575	0.001

High removal efficiency of fluoride (72%) was obtained at 1.5 g/L in acidic media within an hour. From the graph observed at 1.5g/L dose of an adsorbent the removal efficiency increases with time.

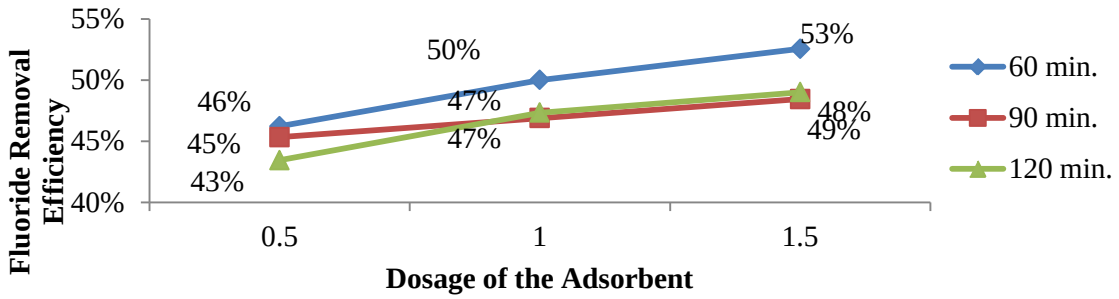


Figure 4:13 Effect dose on adsorption efficiency at pH 6.5.

Figure 4:13 showed that the highest removal of fluoride 53% was obtained at 1.5 g/L in 60 min in neutral medium; with increasing of contact time to 90 and 120 min for the same dosages were 48% and 49% removal respectively. Similar situation was observed at pH 6.5, where the fluoride removal efficiency increased when dosage increased. Even though the results insignificantly varied between the contact time of 90 and 120 min, the same trend was observed that the removal increases when dosage increases.

Table 4:17 ANOVA of dose effects at constant pH 6.5

pH*Dose*Time	Coefficients	P-Value
6.5 0.5 60	1.267	0.006
6.5 0.5 90	-0.657	0.147
6.5 0.5 120	-0.61	0.177
6.5 1.0 60	-0.61	0.177
6.5 1.0 90	0.43	0.340
6.5 1.0 120	0.18	0.688
6.5 1.5 60	-0.657	0.147
6.5 1.5 90	0.227	0.613
6.5 1.5 120	0.43	0.340

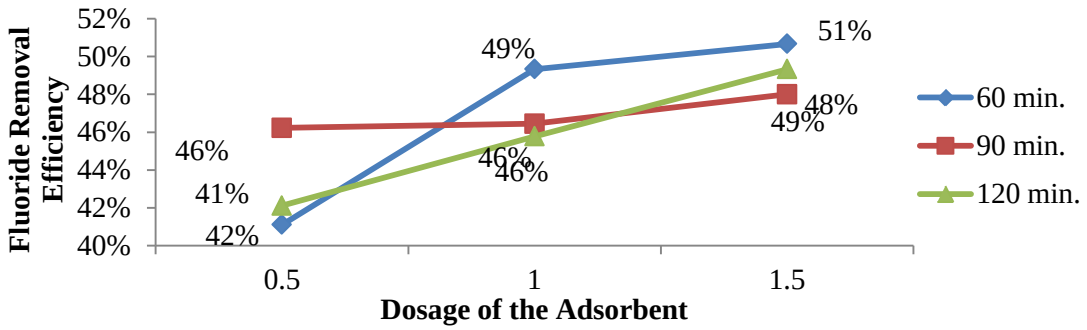


Figure 4:14 Effect dose effect on adsorption efficiency at pH 9.

The fluoride adsorption was highly dependent on the dosage. The results show on figure 4:14 that as the dosage increase; the removal efficiency of fluoride also increases. In this study, the removal efficiency of fluoride showed increase at basic (pH 9) media when dose increased in every contact time. A similar case was observed at the basic media that the removal efficiency was low (Asheesh et al, 2012).

Table 4:18 ANOVA of dose effects at constant pH 9

pH*Dose*Time	Coefficients	P-Value
9.0 0.5 60	-0.573	0.204
9.0 0.5 90	0.948	0.038
9.0 0.5 120	-0.375	0.404
9.0 1.0 60	1.032	0.024
9.0 1.0 90	-0.262	0.560
9.0 1.0 120	-0.77	0.090
9.0 1.5 60	-0.459	0.308
9.0 1.5 90	-0.686	0.130
9.0 1.5 120	1.146	0.013

From the graphs fig 4:12-4:14, an increase of adsorbent dose will increase the adsorbate-adsorbent interaction as a result of increasing surface area of the adsorbent. This might be because by increasing dosage, more surface sites and pore volume would be available for fluoride to be adsorbed. With an increased adsorbent higher adsorption capacity for activated carbon was also reported (Asheesh et al, 2012; Poudyal and Babel 2015). For more details on ANOVA see (Appendix B-6).

4.3. Kinetics adsorption models

The kinetic adsorption of fluoride was determined using both pseudo first order and second order mechanisms using 100ml of 30 mg/L fluoride concentration solution and best selected pH value (pH 2), and 1.5 g/L dosage of adsorbent and stir with magnetic stirrer at 120 rpm. The sample solution was taken every 20 minute interval, and analyzed for defouridation. From the figure 4.15 observed that maximum adsorption was obtained at the 60th minute which is in good agreement with the batch adsorption experiment.

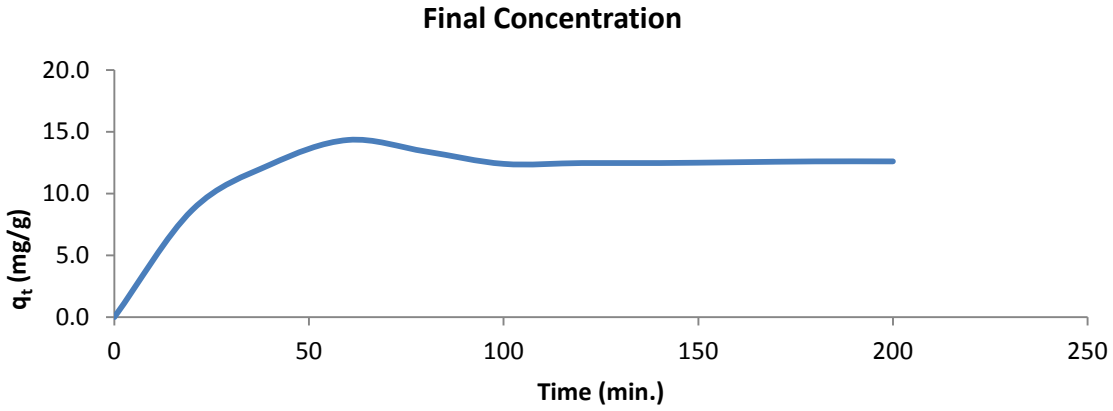


Figure 4:15 Rate of adsorption of fluoride (q_t)with activated carbon of *Catha edulis*

Pseudo first order kinetics

The pseudo first order was conducted using the derived and linearized equation;

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t$$

From the table 4:3 below every adsorption capacity at each interval of contact time was determined. Using the results graph log ($q_e - q_t$) versus t was plotted to determine K_t, q_e, and correlation coefficient (R^2).

Table 4:19 Experimental data for pseudo first order kinetics model

Time (min.)	q_t	Log ($q_e - q_t$)
0	0.0	1.1
20	8.7	0.6
40	12.3	-1.2
60	14.3	----
80	13.4	----
100	12.4	----
120	12.5	----
140	12.5	----
160	12.5	----
180	12.6	----
200	12.6	----

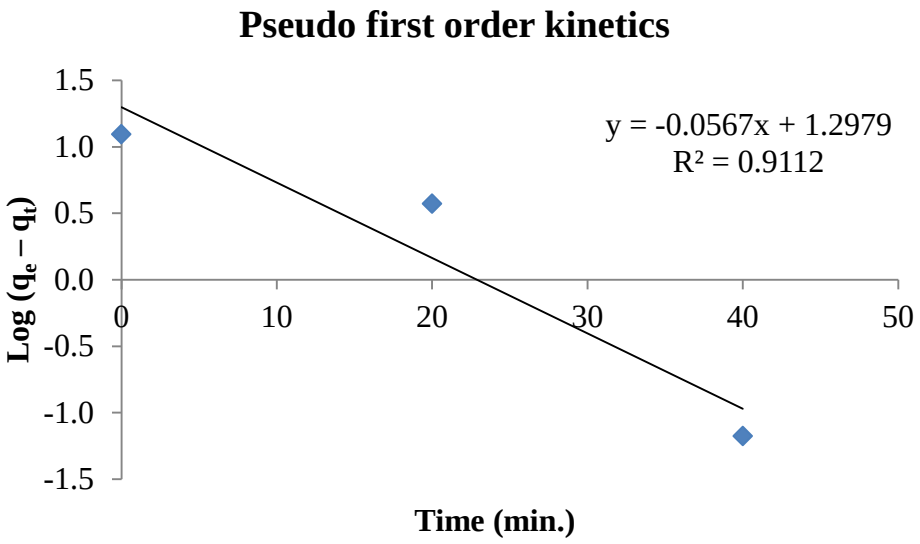


Figure 4:16 Graph of pseudo first order kinetics model.

The figure 4:16 above shows that the correlation coefficient (R^2) from the graph pseudo first order kinetics was 0.911, as indicated in the methodology on equation (9), the constant term can be expressed as Log (q_e) and its value is 1.2979, and K_1 is 0.1306, then this result compared with pseudo second order kinetics (R^2) and the best fit would be selected. 0.911 means the correlation coefficient is close to 1, which means its almost

close to the predicted data. It also meant that 0.099 is an error conducted by the unknown and uncontrolled factors.

Pseudo second order kinetics

The derived and linearized equation below was used in pseudo second order kinetic model;

$$\left[\frac{t}{q_t}\right] = \frac{1}{k_2 qe^2} + \frac{1}{q_e}(t)$$

Similar to pseudo first order kinetics, the table 4-3 below shows the experimental data conducted to determine the adsorption rate, and a graph of t/q versus t plot was drawn to determine the slope and intercept values the pseudo second order kinetics R^2, K_2 and Intercept ($1/K_2q_e^2$).

Table 4:20 Experimental data for pseudo second order kinetic model

Time (min.)	**q_t**	**t/q_t**
0	0.0	0.0
20	8.7	2.3
40	12.3	3.2
60	14.3	4.2
80	13.4	6.0
100	12.4	8.1
120	12.5	9.6
140	12.5	11.2
160	12.5	12.8
180	12.6	14.3
200	12.6	15.9

By plotting (t/q_t) and t, qe and k_2 was determined in a linear relationship from slop and intercept respectively.

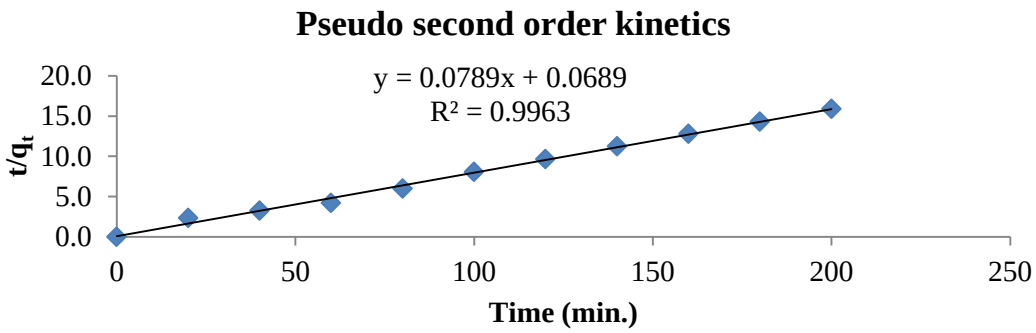


Figure 4:17 Pseudo second order kinetics model.

The result shown from the above figure 4-17, based on the equation given in the methodology section (12), intercept ($1/K_2qe^2$) is 0.0689; hence K_2 is 0.0904. Correlation coefficient (R^2) of pseudo second order kinetics was found to be 0.996 from the given graph, which is greater than first order R^2 (0.9112). Here the 0.004 is also conducted by the unknown and uncontrolled factors. Conformity between experimental data and the models predicted values were expressed by correlation coefficient which is close to 1. Therefore pseudo second order kinetics model is chosen as a best fit model. The same condition also reported when an experiment was conducted using pine wood and pine bark (Mohan et al, 2012).

4.4.Isotherm adsorption models

The adsorption isotherm is determined by varying doses (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 g/L) of adsorbent were applied to constant fluoride concentration (30 mg/L), and selected factor of pH 2 for 60 min. The adsorption data were conducted at a room temperature and analyzed the amount of solute adsorbed per unit of adsorbent (q) as a function of the equilibrium concentration of the solute in the bulk solution (C_e), using of both Freundlich and Langmuir isotherm models. The adsorption capacity analyses is mostly investigated by using both Langmuir and Freundlich isotherm equations and chosen the best fit (Sharma, 2012). The table below showed the final concentration of elute for each dose obtained during the experiment.

Table 4:21 Data collection for isotherm models

Dose(g/L)	C_e (mg/L)
0.5	15
1	11.5
1.5	8.5
2	7.9
2.5	7.1
3	6.8
3.5	6.1
4	5.7

Langmuir isotherm

By using linearized form of Langmuir;

$$\frac{1}{q} = \frac{1}{q_{\mathrm{m}}} + \left(\frac{1}{bq_{\mathrm{m}}}\right)\left(\frac{1}{C_{\mathrm{e}}}\right)$$

The adsorption is based on assumption of surface of the adsorbent sites is capable of adsorbing one molecule so that the layer of the adsorbent would have a mono layer thickness. Once the molecules occupied the sites, there will be no further adsorption occur (Voudrias et al. 2002). Langmuir isotherm was determined by plotting ($1/q_e$) versus ($1/C_e$) and the maximum adsorption capacity (q_m), Langmuir isotherm constant (b) and R^2 were determined from the graph.

Table 4:22 Langmuir isotherm model calculated data

$1/C_e$	$1/q_e$
0.07	0.03
0.09	0.05
0.12	0.07
0.13	0.09
0.14	0.11
0.15	0.13
0.16	0.15
0.18	0.16

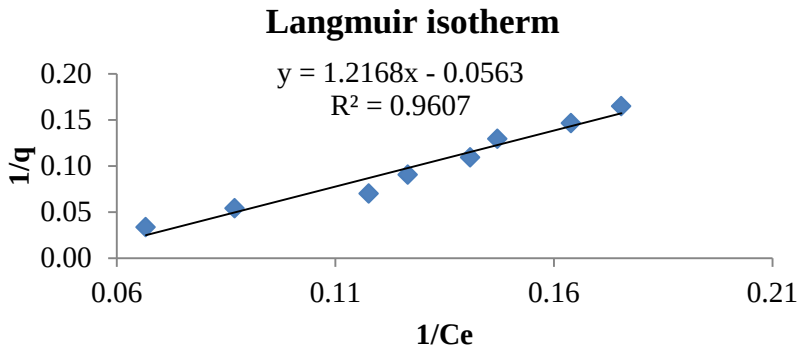


Figure 4:18 Langmuir isotherm model

The figure 4-18 above showed the Langmuir's adsorption constants (b) is 0.05, maximum adsorption capacity (q_m) is 17.86 mg/g, and correlation coefficient (R^2) is 0.9607.

Freundlich isotherm

By using linerarized form of Freundlich equation;

$$logq = logKf + \frac{1}{n}\log Ce$$

Freundlich is based on the assumption of heterogeneous surface composing different sites for adsorption. It doesn't forecast the adsorbent's saturation of the adsorbate, which implies multilayer sorption of the surface sites. The graph was conducted by plotting log q_e and log C_e. The values of K_f and n were obtained from equation (14), i.e the slope (1/n) and intercept value (log K_f) (Alagumuthu et al, 2010b).

Table 4:23 Freundlich isotherm model calculated data

Log C_e	**Log q_e**
1.18	1.48
1.06	1.27
0.93	1.16
0.90	1.04
0.85	0.96
0.83	0.89
0.79	0.83
0.76	0.78

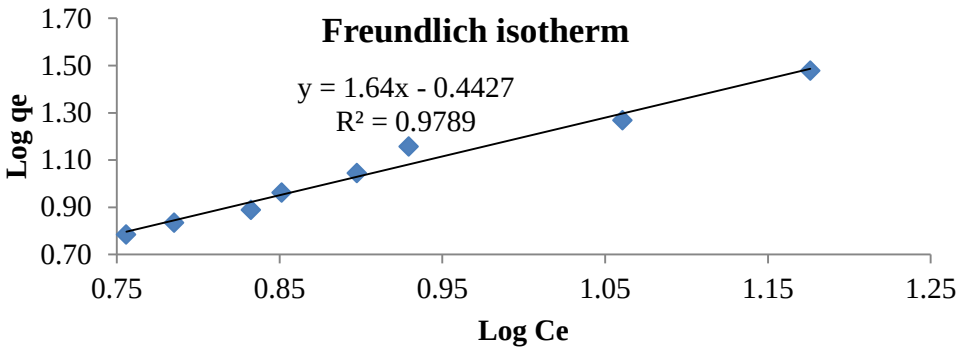


Figure 4:19 Freundlich adsorption isotherm model at room temperature.

The above figures 4:19 of adsorption isotherm showed the relationship of between bulk aqueous concentration of fluoride (adsorbate) and the adsorbed on the adsorbent. Freundlich's intensity (n) is 0.61, Freundlich equilibrium constant/adsorption capacity (K_f) is 0.094, and R^2 is 0.9789 was obtained. The R^2 value of Freundlich model (0.98) is greater than Langmuir (0.96) isotherm model. By observing the intensity (1/n) the value is below 1 which indicates that adsorption system is low in heterogeneity. This might imply chemosorption process as 1/n increases beyond 1; which it indicates cooperative adsorption (Shahbeig et al, 2013). However, the correlation coefficient of Langmuir's model showed lower than Freundlich's, maximum adsorption capacity (17.86) indicating a good adsorption capacity of the adsorbent (Sinha et al. 2003; Karthikeyan and Llango 2007; Jamode et al. 2004; Mohan et al. 2012; Alagumuthu and Rajan 2010b; Alagumuthu et al 2011; Asheesh et al, 2012). The effect of isotherm adsorption shape can be used to predict whether the system is 'favorable' or 'unfavorable' (Tan et.al. 2009) using the essential features of the Langmuir isotherm of a dimensionless constant separation factor or equilibrium parameter R_L which is defined by the following relationship;

$$R_L = \frac{1}{1+bC_o} \quad (18)$$

Where,

R_L is a dimensionless separation factor,

C_O the initial fluoride concentration (mg/L) and

b the Langmuir constant (L/mg).

So, by substituting b=0.05, and C_o=30mg/L

$$R_L = \frac{1}{1 + (0.05 * 30)}$$

$R_{L=}0.4$

The parameter R_L indicates the isotherm shape when $R_L>1$ (unfavorable); $R_L=1$ (Linear); $0<R_L<1$ (favorable); and when $R_L=0$ (Irreversible). Based on equation (18) the value of dimensionless separation factor (R_L), 0.4, which indicate a favorable adsorption condition (Mohan et al, 2012).

4.5. Fluoride removal efficiency versus fluoride Removal capacity

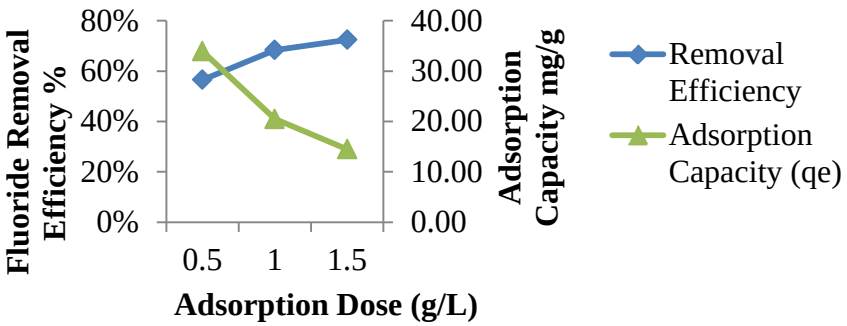


Figure 4:20 Fluoride removal efficiency Vs adsorption capacity at contact time 60 min. in acidic (pH 2) media.

As shown from figure 4-20 above, when the adsorbent dosage increases the fluoride removal efficiency increases but the fluoride adsorption capacity decreases. See (Appendix C-2), the fluoride concentration in the solution started to decrease after the adsorption process started, so whenever the dose increases, the fluoride concentration decreases due to availability of free sites for adsorption. Therefore from the figures shown above the capacity decreases due to high dosage of adsorbent for the ion binding sites and no available fluoride ions to remain in the solution (Ahmedin, 2007).

4.6.Continuous flow fixed bed reactor

Continuous flow was conducted in a column for fluoride adsorption by using best selected factors 1.5 g/L, pH 2. The continuous flow was simulated by allowing the flow rate at 2 ml/min with a constant concentration of fluoride 30 mg/L so that the adsorption process will take its time for the adsorbate to pass through the bed. Studies pointed out that by using low flow rate such as 2 ml/min the adsorption process would be efficient. Higher flow rate would decrease the residence time restricting the contact time of aqueous solution with the adsorbent, hence the fluoride ions would diffuse and exits the column before it have the chance to be adsorbed (Ahmedin, 2007; Iman et al., 2013). The table

below showed the final concentration, capacity, and removal efficiency of fluoride. Starting from 30 min., the residual fluoride was observed to be 2.2 mg/L of $C_{f,}$ where the removal efficiency started with 93%.

Table 4:24 Data collection and calculation from countinous flow

Time (min.)	C_f mg/L	q_t (mg/g)	Removal Efficiency %	ml	Hour
30	2.2	18.5	93%	60	0.5
60	2.5	18.3	92%	120	1
90	2.8	18.1	91%	180	1.5
120	2.8	18.1	91%	240	2
150	2.8	18.1	91%	300	2.5
180	3.1	17.9	90%	360	3
210	3.1	17.9	90%	420	3.5
240	3.2	17.9	89%	480	4
270	4.1	17.3	86%	540	4.5
300	4.9	16.7	84%	600	5
330	7	15.3	77%	660	5.5
360	9.1	13.9	70%	720	6
390	11	12.7	63%	780	6.5
420	15	10.0	50%	840	7
450	17	8.7	43%	900	7.5
480	20	6.7	33%	960	8
510	22	5.3	27%	1020	8.5
540	25	3.3	17%	1080	9
570	27	2.0	10%	1140	9.5
600	29	0.7	3%	1200	10
630	30	0.0	0%	1260	10.5
660	30	0.0	0%	1320	11

In continuous fixed bed adsorption system, the profile of fluoride concentration varies in time. The figure has three phases where in the first 240-270 min adsorption of fluoride ion takes place with removal fluoride efficiency of 93%-90%. As time goes on from 240 to 600 min. (4 hrs. to 10 hrs.) the adsorption decrease with the increase of time and finally adsorption becomes negligible. This is due to the exhaustion of the adsorbent. Similar situation was observed when using cashew nut sheath AC in continuous flow and it extended to 4hr then the residual fluoride concentration started to increases (Sivabalan, et al,2003), in lead ion adsorption with activated carbon of palm shell (Issabayeva et al.,2008). Therefore, an efficient adsorption (90% and above) could be attained with low flow rate of adsorbate through the activated carbon.

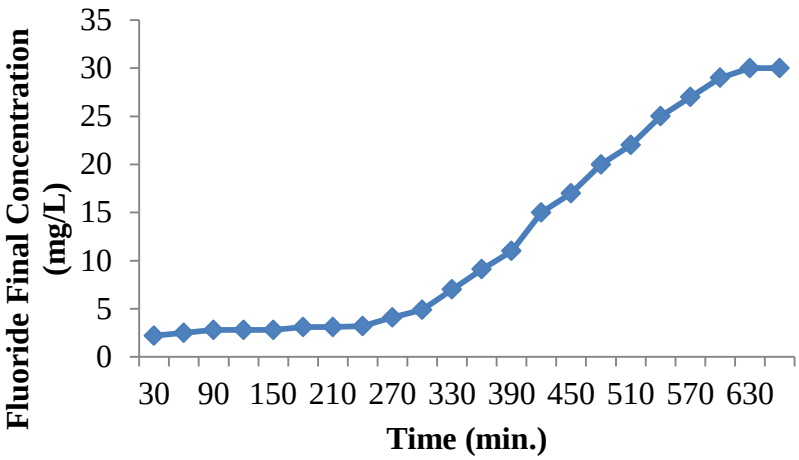


Figure 4:21 Fixed bed continous flow fluoride adsorption

5. CONCLUSION AND RECOMMENDATION

Conclusion

In this study, production of samples using different chemicals and temperature for activation purpose showed a significant result on pore volumes and fixed carbon content. Activated carbon produced from (H_2SO_4) and (H_3PO_4) used as an impregnating agent were found to be higher in bulk density which indirectly meant they have low porosity. It was also obtained that the p-value of bulk density was highly significant (P=0.000) except for the H_3PO_4 and 500°C (P=0.646), which indicate highly insignificant. The activated carbon produced using KOH at 550°C was found to be better with lower bulk density and higher fixed carbon content than the other product samples.

In the adsorption, process the three factors (dose, pH and contact time) was conducted with the selected activated carbon at different level of pH (2, 6.5, and 9), Dose (0.5, 1.0, and 1.5 g/L), and Contact time (60, 90, and 120 min.) in a batch process. Hence the results was observed to be most significant in fluoride removal efficiency, and the highest adsorption was found to at acidic media pH 2 aquatic solution by adjusting the pH using NaOH and HNO_3, and using 1.5 g/L of adsorbent for an hour. Hence fluoride was adsorbed up to 72.4% the fluoride ions and it has a highly significant value (p=0.015). Fluoride adsorption seemed to increase when the amount of adsorbent increased from dose 0.5 to 1.5 g/L.

Adsorption capacity also seemed to be affected when the adsorption efficiency increased, the capacity started to decrease since the site area would be loaded and no available free space for the fluoride adsorption would take place.

Considering Adsorption isotherm, both Langumuir and Freundlich isotherms were studied and the fluoride adsorption efficiency was found to be better fitted using Freundlich isotherm model. Kinetics studies were also studied by using both pseudo first and second order equations and found that the fluoride adsorption was well fitted to the second order kinetics.

Selected factor after the laboratory batch experiment and statistical analysis, 1.5, pH at 2 media for 60 min was used in fixed bed column continuous flow and obtained a good adsorption from 30 min to 4 hr, and then the fluoride concentration started to increase.

In conclusion, *Catha edulis* was observed to be a good adsorbent and have a good adsorption capacity. And this experiment also indicates by adding more adsorbent, the removal efficiency could be improved to a better standard. This in return, show that production of activated carbon from *Catha edulis* have dual role in minimizing environmental pollution instead of discarding as waste or burning and at the same time also in removal of fluoride from water.

Recommendation

In this finding,

- KOH activated carbon a good activated carbon, so this can be tested for adsorption capacity of other pollutant species. By changing the aqueous solution pH media, the activated carbon might show capacity in adsorbing cationic pollutants.
- The initial fluoride concentration was fixed through all the experiments, therefore further research should be undertaken at different fluoride concentration. So that after further investigation, this could be applied on surface water, ground water and even waste water.
- Acidic media was found to be better for fluoride adsorption than neutral and basic media; this is due to functional group of surface of the adsorbent. So further to investigation should be taken by either using different chemical or physical activation methods in order to establish an appropriate pH.
- Regeneration process should be investigated to either reuse the sample or safely disposal in economic and environmental safe manner.

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7. APPENDIX (CES)

Appendix A-1 : Detail calculation for bulk density

Samples	Mass of the Sample (g)	Volume of the Sample(ml)	Bulk Density using the formula D=M/V (Kg/m^3)
H_3PO_4, 500 °C	8.58	23	373.04
	5.56	15	370.67
	7.4	20	370.00
H_3PO_4, 550 °C	9.86	24	410.83
	7	17	411.76
	12.4	30.5	406.56
H_3PO_4, 600 °C	6.972	18	387.33
	8.91	23	387.39
	11.2	29	386.21
H_2SO_4, 500 °C	5.05	12.5	404.00
	8.1	20	405.00
	6.8	17	400.00
H_2SO_4, 550 °C	11.3	24.5	461.22
	9.62	21	458.10
	7.9	17	464.71
H_2SO_4, 600 °C	7.52	16.5	455.76
	8.25	18	458.33
	11.4	25	456.00
KOH, 500 °C	9.81	45.5	215.60
	4	18.5	216.22
	6.7	31	216.13
KOH, 550 °C	2.75	13.2	208.33
	6.05	28.7	210.80
	3.91	18.5	211.35
KOH, 600 °C	4.34	20	217.00
	2.45	11.5	213.04
	3.65	17	214.71
Untreated, 550 °C	2.69	7.6	353.95
	3.9	11.2	348.21
	1.96	5.6	350.00

Appendix A-2: Detail calculation of moisture content

Samples	**W1**	**W2**	**Moisture Content %** $= \left[\frac{W1 - W2}{W1}\right] * 100$
H_3PO_4, 500 °C	1	0.872	13%
	1	0.913	9%
	1	0.900	10%
H_3PO_4, 550 °C	1	0.900	10%
	1	0.967	3%
	1	0.930	7%
H_3PO_4, 600 °C	1	0.894	11%
	1	0.938	6%
	1	0.910	9%
H_2SO_4, 500 °C	1	0.900	10%
	1	0.924	8%
	1	0.950	5%
H_2SO_4, 550 °C	1	0.976	2%
	1	0.938	6%
	1	0.970	3%
H_2SO_4, 600 °C	1	0.950	5%
	1	0.950	5%
	1	0.930	7%
KOH, 500 °C	1	0.927	7%
	1	0.918	8%
	1	0.900	10%
KOH, 550 °C	1	0.960	4%
	1	0.962	4%
	1	0.960	4%
KOH, 600 °C	1	0.960	4%
	1	0.970	3%
	1	0.970	3%
Untreated, 550 °C	1	0.970	3%
	1	0.980	2%
	1	0.980	2%

Appendix A-3: Detail calculation of ash content for each sample

Samples	**W1**	**W2**	**Ash %=** $\left[\frac{W2}{W1}\right] * 100$
H_3PO_4, 500 °C	1	0.07	7%
	1	0.07	7%
	1	0.06	6%
H_3PO_4, 550 °C	1	0.076	8%
	1	0.08	8%
	1	0.07	7%
H_3PO_4, 600 °C	1	0.089	9%
	1	0.08	8%
	1	0.08	8%
H_2SO_4, 500 °C	1	0.18	18%
	1	0.19	19%
	1	0.18	18%
H_2SO_4, 550 °C	1	0.17	17%
	1	0.17	17%
	1	0.19	19%
H_2SO_4, 600 °C	1	0.198	20%
	1	0.2	20%
	1	0.2	20%
KOH, 500 °C	1	0.066	7%
	1	0.04	4%
	1	0.04	4%
KOH, 550 °C	1	0.067	7%
	1	0.07	7%
	1	0.08	8%
KOH, 600 °C	1	0.08	8%
	1	0.07	7%
	1	0.07	7%
Untreated, 550 °C	1	0.13	13%
	1	0.14	14%
	1	0.14	14%

Appendix A-4: Volatile content detailed calculations

Samples	**W1**	**W2**	**VC%= $\left[\frac{W1-W2}{W1}\right] * 100$**
H_3PO_4, 500 °C	1	0.642	36%
	1	0.64	36%
	1	0.66	34%
H_3PO_4, 550 °C	1	0.727	27%
	1	0.7	30%
	1	0.73	27%
H_3PO_4, 600 °C	1	0.73	27%
	1	0.73	27%
	1	0.72	28%
H_2SO_4, 500 °C	1	0.69	31%
	1	0.69	31%
	1	0.68	32%
H_2SO_4, 550 °C	1	0.74	26%
	1	0.75	25%
	1	0.74	26%
H_2SO_4, 600 °C	1	0.75	25%
	1	0.75	25%
	1	0.78	22%
KOH, 500 °C	1	0.739	26%
	1	0.75	25%
	1	0.71	29%
KOH, 550 °C	1	0.8	20%
	1	0.8	20%
	1	0.8	20%
KOH, 600 °C	1	0.8	20%
	1	0.79	21%
	1	0.79	21%
Untreated, 550 °C	1	0.78	22%
	1	0.8	20%
	1	0.79	21%

Summarized characterization of the samples

Samples	Moisture Content%	Volatile Content%	Ash Content %	Fixed Carbon %	Bulk Density(Kg/M^3)
H_3PO_4, 500 °C	13%	36%	7%	44.4%	373.04
	9%	36%	7%	48.3%	370.67
	10%	34%	6%	50.0%	370.00
H_3PO_4, 550 °C	10%	27%	8%	55.1%	410.83
	3%	30%	8%	58.7%	411.76
	7%	27%	7%	59.0%	406.56
H_3PO_4, 600 °C	11%	27%	9%	53.5%	387.33
	6%	27%	8%	58.8%	387.39
	9%	28%	8%	55.0%	386.21
H_2SO_4, 500 °C	10%	31%	18%	41.0%	404.00
	8%	31%	19%	42.4%	405.00
	5%	32%	18%	45.0%	400.00
H_2SO_4, 550 °C	2%	26%	17%	54.6%	461.22
	6%	25%	17%	51.8%	458.10
	3%	26%	19%	52.0%	464.71
H_2SO_4, 600 °C	5%	25%	20%	50.2%	455.76
	5%	25%	20%	50.0%	458.33
	7%	22%	20%	51.0%	456.00
KOH, 500 °C	7%	26%	7%	60.0%	215.60
	8%	25%	4%	62.8%	216.22
	10%	29%	4%	57.0%	216.13
KOH, 550 °C	4%	20%	7%	69.3%	208.33
	4%	20%	7%	69.2%	210.80
	4%	20%	8%	68.0%	211.35
KOH, 600 °C	4%	20%	8%	68.0%	217.00
	3%	21%	7%	69.0%	213.04
	3%	21%	7%	69.0%	214.71
Untreated, 550 °C	3%	22%	13%	64.0%	353.95
	2%	20%	14%	63.0%	348.21
	2%	21%	14%	63.0%	350.00

Appendix B-1: Fixed carbon versus chemicals, temperature

Factor Information

Factor	Levels	Values
Chemicals	3	H2So4, H3Po4, KOH
Temperature	3	500, 550, 600

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.188890	0.023611	57.88	0.000
Linear	4	0.188472	0.047118	115.51	0.000
Chemicals	2	0.139801	0.069900	171.36	0.000
Temperature	2	0.048671	0.024335	59.66	0.000
2-Way Interactions	4	0.000419	0.000105	0.26	0.902
Chemicals*Temperature	4	0.000419	0.000105	0.26	0.902
Error	18	0.007342	0.000408		
Total	26	0.196233			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0201969	96.26%	94.60%	91.58%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.56044	0.00389	144.19	0.000	
Chemicals					
H2So4	-0.07370	0.00550	-13.41	0.000	1.33
H3Po4	-0.02391	0.00550	-4.35	0.000	1.33
KOH	0.09762	0.00550	17.76	0.000	*
Temperature					
500	-0.05944	0.00550	-10.81	0.000	1.33
550	0.03705	0.00550	6.74	0.000	1.33
600	0.02239	0.00550	4.07	0.001	*
Chemicals*Temperature					
H2So4 500	0.00084	0.00777	0.11	0.915	1.78
H2So4 550	0.00428	0.00777	0.55	0.589	1.78
H2So4 600	-0.00512	0.00777	-0.66	0.518	*
H3Po4 500	-0.00140	0.00777	-0.18	0.859	1.78
H3Po4 550	0.00249	0.00777	0.32	0.752	1.78
H3Po4 600	-0.00110	0.00777	-0.14	0.890	*
KOH 500	0.00056	0.00777	0.07	0.944	*
KOH 550	-0.00677	0.00777	-0.87	0.395	*
KOH 600	0.00622	0.00777	0.80	0.434	*

Appendix B-2: Moisture content versus chemicals, temperature

Factor Information

Factor	Levels	Values
Chemicals	3	H2So4, H3Po4, KOH
Temperature	3	500, 550, 600

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.014936	0.001867	4.83	0.003
Linear	4	0.013768	0.003442	8.91	0.000
Chemicals	2	0.006005	0.003003	7.77	0.004
Temperature	2	0.007763	0.003881	10.05	0.001
2-Way Interactions	4	0.001168	0.000292	0.76	0.567
Chemicals*Temperature	4	0.001168	0.000292	0.76	0.567
Error	18	0.006954	0.000386		
Total	26	0.021890			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0196558	68.23%	54.11%	28.52%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.06519	0.00378	17.23	0.000	
Chemicals					
H2So4	-0.00837	0.00535	-1.56	0.135	1.33
H3Po4	0.02095	0.00535	3.92	0.001	1.33
KOH	-0.01258	0.00535	-2.35	0.030	*
Temperature					
500	0.02326	0.00535	4.35	0.000	1.33
550	-0.01668	0.00535	-3.12	0.006	1.33
600	-0.00658	0.00535	-1.23	0.235	*
Chemicals*Temperature					
H2So4 500	-0.00488	0.00757	-0.65	0.527	1.78
H2So4 550	-0.00154	0.00757	-0.20	0.841	1.78
H2So4 600	0.00642	0.00757	0.85	0.407	*
H3Po4 500	-0.00442	0.00757	-0.58	0.567	1.78
H3Po4 550	-0.00186	0.00757	-0.25	0.808	1.78
H3Po4 600	0.00628	0.00757	0.83	0.417	*
KOH 500	0.00930	0.00757	1.23	0.235	*
KOH 550	0.00340	0.00757	0.45	0.658	*
KOH 600	-0.01270	0.00757	-1.68	0.110	*

Appendix B-3: Volatile content versus chemicals, temperature

Factor Information

Factor	Levels	Values
Chemicals	3	H2So4, H3Po4, KOH
Temperature	3	500, 550, 600

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.056009	0.007001	50.22	0.000
Linear	4	0.055425	0.013856	99.39	0.000
Chemicals	2	0.027480	0.013740	98.56	0.000
Temperature	2	0.027945	0.013973	100.23	0.000
2-Way Interactions	4	0.000583	0.000146	1.05	0.411
Chemicals*Temperature	4	0.000583	0.000146	1.05	0.411
Error	18	0.002509	0.000139		
Total	26	0.058518			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0118071	95.71%	93.81%	90.35%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.26563	0.00227	116.90	0.000	
Chemicals					
H2So4	0.00437	0.00321	1.36	0.191	1.33
H3Po4	0.03670	0.00321	11.42	0.000	1.33
KOH	-0.04107	0.00321	-12.78	0.000	*
Temperature					
500	0.04537	0.00321	14.12	0.000	1.33
550	-0.01974	0.00321	-6.14	0.000	1.33
600	-0.02563	0.00321	-7.98	0.000	*
Chemicals*Temperature					
H2So4 500	-0.00204	0.00454	-0.45	0.659	1.78
H2So4 550	0.00641	0.00454	1.41	0.176	1.78
H2So4 600	-0.00437	0.00454	-0.96	0.349	*
H3Po4 500	0.00496	0.00454	1.09	0.289	1.78
H3Po4 550	-0.00159	0.00454	-0.35	0.730	1.78
H3Po4 600	-0.00337	0.00454	-0.74	0.468	*
KOH 500	-0.00293	0.00454	-0.64	0.528	*
KOH 550	-0.00481	0.00454	-1.06	0.303	*
KOH 600	0.00774	0.00454	1.70	0.106	*

Appendix B-4: Ash content versus chemicals, temperature

Factor Information

Factor	Levels	Values
Chemicals	3	H2So4, H3Po4, KOH
Temperature	3	500, 550, 600

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	0.084366	0.010546	169.89	0.000
Linear	4	0.083611	0.020903	336.74	0.000
Chemicals	2	0.081981	0.040991	660.35	0.000
Temperature	2	0.001630	0.000815	13.13	0.000
2-Way Interactions	4	0.000755	0.000189	3.04	0.045
Chemicals*Temperature	4	0.000755	0.000189	3.04	0.045
Error	18	0.001117	0.000062		
Total	26	0.085483			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0078787	98.69%	98.11%	97.06%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.10874	0.00152	71.72	0.000	
Chemicals					
H2So4	0.07770	0.00214	36.24	0.000	1.33
H3Po4	-0.03374	0.00214	-15.73	0.000	1.33
KOH	-0.04396	0.00214	-20.50	0.000	*
Temperature					
500	-0.00919	0.00214	-4.28	0.000	1.33
550	-0.00063	0.00214	-0.29	0.772	1.33
600	0.00981	0.00214	4.58	0.000	*
Chemicals*Temperature					
H2So4 500	0.00607	0.00303	2.00	0.060	1.78
H2So4 550	-0.00915	0.00303	-3.02	0.007	1.78
H2So4 600	0.00307	0.00303	1.01	0.324	*
H3Po4 500	0.00085	0.00303	0.28	0.782	1.78
H3Po4 550	0.00096	0.00303	0.32	0.754	1.78
H3Po4 600	-0.00181	0.00303	-0.60	0.557	*
KOH 500	-0.00693	0.00303	-2.28	0.035	*
KOH 550	0.00819	0.00303	2.70	0.015	*
KOH 600	-0.00126	0.00303	-0.42	0.683	*

Appendix B-5: Bulk density versus chemicals, temperature

Factor Information

Factor	Levels	Values
Chemicals	3	H2So4, H3Po4, KOH
Temperature	3	500, 550, 600

α to enter = 0.15, α to remove = 0.15

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	263080	32885	7931.54	0.000
Linear	4	258957	64739	15614.48	0.000
Chemicals	2	254468	127234	30687.56	0.000
Temperature	2	4489	2245	541.40	0.000
2-Way Interactions	4	4123	1031	248.59	0.000
Chemicals*Temperature	4	4123	1031	248.59	0.000
Error	18	75	4		
Total	26	263154			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.03620	99.97%	99.96%	99.94%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	347.781	0.392	887.50	0.000	
Chemicals					
H2So4	92.565	0.554	167.03	0.000	1.33
H3Po4	41.529	0.554	74.94	0.000	1.33
KOH	-134.094	0.554	-241.97	0.000	*
Temperature					
500	-17.708	0.554	-31.95	0.000	1.33
550	12.626	0.554	22.78	0.000	1.33
600	5.082	0.554	9.17	0.000	*
Chemicals*Temperature					
H2So4 500	-19.638	0.784	-25.06	0.000	1.78
H2So4 550	8.370	0.784	10.68	0.000	1.78
H2So4 600	11.269	0.784	14.38	0.000	*
H3Po4 500	-0.366	0.784	-0.47	0.646	1.78
H3Po4 550	7.782	0.784	9.93	0.000	1.78
H3Po4 600	-7.416	0.784	-9.46	0.000	*
KOH 500	20.004	0.784	25.52	0.000	*
KOH 550	-16.151	0.784	-20.61	0.000	*
KOH 600	-3.853	0.784	-4.92	0.000	*

Appendix B-6: ANOVA

Removal efficiency versus dose, pH, time

Factor	Type	Levels	Values
Dose	fixed	3	0.5, 1.0, 1.5
pH	fixed	3	2.0, 6.5, 9.0
Time	fixed	3	60, 90, 120

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	26	6015.47	231.36	114.89	0.000
Linear	6	5724.07	954.01	473.72	0.000
Dose	2	777.16	388.58	192.95	0.000
pH	2	4828.13	2414.07	1198.72	0.000
Time	2	118.78	59.39	29.49	0.000
2-Way Interactions	12	247.06	20.59	10.22	0.000
Dose*pH	4	115.99	29.00	14.40	0.000
Dose*Time	4	98.15	24.54	12.18	0.000
pH*Time	4	32.91	8.23	4.09	0.006
3-Way Interactions	8	44.35	5.54	2.75	0.013
Dose*pH*Time	8	44.35	5.54	2.75	0.013
Error	54	108.75	2.01		
Total	80	6124.22			

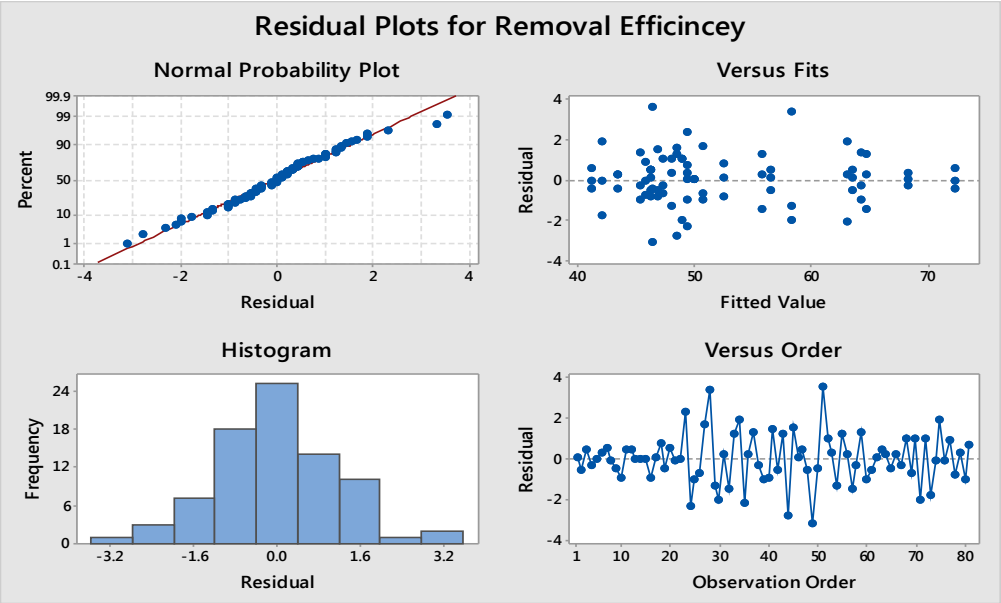
Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
1.41911	98.22%	97.37%	96.00%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value
Constant	52.573	0.158	333.42	0.000
Dose				
0.5	-4.227	0.223	-18.96	0.000
1.0	1.119	0.223	5.02	0.000
1.5	3.109	0.223	13.94	0.000
pH				
2.0	10.899	0.223	48.88	0.000
6.5	-4.881	0.223	-21.89	0.000
9.0	-6.017	0.223	-26.98	0.000
Time				
60	1.563	0.223	7.01	0.000
90	-0.175	0.223	-0.79	0.435
120	-1.388	0.223	-6.22	0.000
Dose*pH				
0.5 2.0	-2.356	0.315	-7.47	0.000
0.5 6.5	1.536	0.315	4.87	0.000
0.5 9.0	0.820	0.315	2.60	0.012
1.0 2.0	1.225	0.315	3.88	0.000
1.0 6.5	-0.736	0.315	-2.33	0.023
1.0 9.0	-0.489	0.315	-1.55	0.127
1.5 2.0	1.131	0.315	3.59	0.001
1.5 6.5	-0.800	0.315	-2.54	0.014
1.5 9.0	-0.331	0.315	-1.05	0.299
Dose*Time				
0.5 60	-1.946	0.315	-6.17	0.000
0.5 90	1.793	0.315	5.68	0.000
0.5 120	0.153	0.315	0.49	0.629
1.0 60	0.635	0.315	2.01	0.049
1.0 90	-0.812	0.315	-2.58	0.013

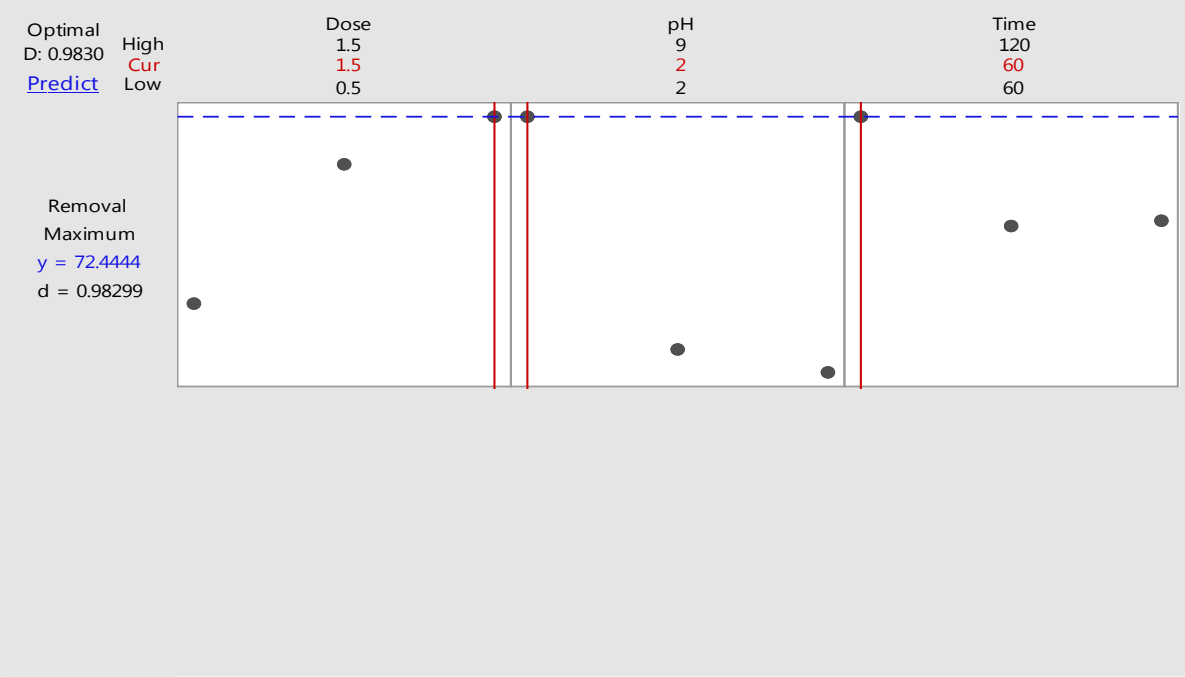
	1.0 120	0.178	0.315	0.56	0.575
	1.5 60	1.311	0.315	4.16	0.000
	1.5 90	-0.980	0.315	-3.11	0.003
	1.5 120	-0.331	0.315	-1.05	0.299
pH*Time					
	2.0 60	0.743	0.315	2.36	0.022
	2.0 90	0.119	0.315	0.38	0.709
	2.0 120	-0.862	0.315	-2.73	0.008
	6.5 60	0.338	0.315	1.07	0.288
	6.5 90	-0.627	0.315	-1.99	0.052
	6.5 120	0.289	0.315	0.92	0.364
	9.0 60	-1.081	0.315	-3.43	0.001
	9.0 90	0.509	0.315	1.61	0.113
	9.0 120	0.573	0.315	1.82	0.075
Dose*pH*Time					
	0.5 2.0 60	-0.694	0.446	-1.56	0.126
	0.5 2.0 90	-0.291	0.446	-0.65	0.516
	0.5 2.0 120	0.985	0.446	2.21	0.031
	0.5 6.5 60	1.267	0.446	2.84	0.006
	0.5 6.5 90	-0.657	0.446	-1.47	0.147
	0.5 6.5 120	-0.610	0.446	-1.37	0.177
	0.5 9.0 60	-0.573	0.446	-1.28	0.204
	0.5 9.0 90	0.948	0.446	2.13	0.038
	0.5 9.0 120	-0.375	0.446	-0.84	0.404
	1.0 2.0 60	-0.422	0.446	-0.95	0.348
	1.0 2.0 90	-0.168	0.446	-0.38	0.708
	1.0 2.0 120	0.590	0.446	1.32	0.191
	1.0 6.5 60	-0.610	0.446	-1.37	0.177
	1.0 6.5 90	0.430	0.446	0.96	0.340
	1.0 6.5 120	0.180	0.446	0.40	0.688
	1.0 9.0 60	1.032	0.446	2.31	0.024
	1.0 9.0 90	-0.262	0.446	-0.59	0.560
	1.0 9.0 120	-0.770	0.446	-1.73	0.090
	1.5 2.0 60	1.116	0.446	2.50	0.015
	1.5 2.0 90	0.459	0.446	1.03	0.308
	1.5 2.0 120	-1.575	0.446	-3.53	0.001
	1.5 6.5 60	-0.657	0.446	-1.47	0.147
	1.5 6.5 90	0.227	0.446	0.51	0.613
	1.5 6.5 120	0.430	0.446	0.96	0.340
	1.5 9.0 60	-0.459	0.446	-1.03	0.308
	1.5 9.0 90	-0.686	0.446	-1.54	0.130
	1.5 9.0 120	1.146	0.446	2.57	0.013



Appendix B-7: Response optimization: removal efficiency

```
Parameters
Response                Lower     Target      Upper Weight  Importance
Removal Efficiency  40.3333      73             1           1


Solution
                                  Removal
                                 Efficiency     Composite
Solution  Dose  pH  Time           Fit           Desirability
 1         1.5      2    60       72.4444       0.982993

Multiple Response Prediction

Variable  Setting
Dose      1.5
pH       2
Time      60

Response               Fit     SE Fit       95% CI            95% PI
Removal Efficiency     72.444  0.847  (70.746, 74.143)  (69.047, 75.842)
```

Optimization Plot



Appendix C-1: Actual and predicted values of fluoride removal efficiency

Observation	**Replication**	**Dose**	**pH**	**Time**	***Predicted %***	***Actual %***
1	Trial (1)	0.5	2	60	59.96	56.7
2	Trial (2)	0.5	2	60	59.96	56.0
3	Trial (3)	0.5	2	60	59.96	57.0
4	Trial (1)	1	2	60	63.40	68.0
5	Trial (2)	1	2	60	63.40	68.3
6	Trial (3)	1	2	60	63.40	68.7
7	Trial (1)	1.5	2	60	66.84	73.0
8	Trial (2)	1.5	2	60	66.84	72.3
9	Trial (3)	1.5	2	60	66.84	72.0
10	Trial (1)	0.5	6.5	60	48.80	45.3
11	Trial (2)	0.5	6.5	60	48.80	46.7
12	Trial (3)	0.5	6.5	60	48.80	46.7
13	Trial (1)	1	6.5	60	52.25	50.0
14	Trial (2)	1	6.5	60	52.25	50.0
15	Trial (3)	1	6.5	60	52.25	50.0
16	Trial (1)	1.5	6.5	60	55.69	51.7
17	Trial (2)	1.5	6.5	60	55.69	52.7
18	Trial (3)	1.5	6.5	60	55.69	53.3
19	Trial (1)	0.5	9	60	42.61	40.7
20	Trial (2)	0.5	9	60	42.61	41.7
21	Trial (3)	0.5	9	60	42.61	41.0
22	Trial (1)	1	9	60	46.05	49.3
23	Trial (2)	1	9	60	46.05	51.7
24	Trial (3)	1	9	60	46.05	47.0
25	Trial (1)	1.5	9	60	49.50	49.7
26	Trial (2)	1.5	9	60	49.50	50.0
27	Trial (3)	1.5	9	60	49.50	52.3
28	Trial (1)	0.5	2	90	58.48	61.7
29	Trial (2)	0.5	2	90	58.48	57.0
30	Trial (3)	0.5	2	90	58.48	56.3
31	Trial (1)	1	2	90	61.92	65.0
32	Trial (2)	1	2	90	61.92	63.3
33	Trial (3)	1	2	90	61.92	66.0
34	Trial (1)	1.5	2	90	65.37	66.7
35	Trial (2)	1.5	2	90	65.37	67.0
36	Trial (3)	1.5	2	90	65.37	67.7
37	Trial (1)	0.5	6.5	90	47.33	46.7
38	Trial (2)	0.5	6.5	90	47.33	45.0
39	Trial (3)	0.5	6.5	90	47.33	44.3

Observation	Replication	Dose	pH	Time	*Predicted %*	*Actual %*
40	Trial (1)	1	6.5	90	50.77	46.0
41	Trial (2)	1	6.5	90	50.77	48.3
42	Trial (3)	1	6.5	90	50.77	46.3
43	Trial (1)	1.5	6.5	90	54.22	49.7
44	Trial (2)	1.5	6.5	90	54.22	45.7
45	Trial (3)	1.5	6.5	90	54.22	50.0
46	Trial (1)	0.5	9	90	41.13	46.3
47	Trial (2)	0.5	9	90	41.13	46.7
48	Trial (3)	0.5	9	90	41.13	45.7
49	Trial (1)	1	9	90	44.58	43.3
50	Trial (2)	1	9	90	44.58	46.0
51	Trial (3)	1	9	90	44.58	50.0
52	Trial (1)	1.5	9	90	48.02	49.0
53	Trial (2)	1.5	9	90	48.02	48.3
54	Trial (3)	1.5	9	90	48.02	46.7
55	Trial (1)	0.5	2	120	57.00	57.0
56	Trial (2)	0.5	2	120	57.00	56.0
57	Trial (3)	0.5	2	120	57.00	54.3
58	Trial (1)	1	2	120	60.45	64.0
59	Trial (2)	1	2	120	60.45	65.7
60	Trial (3)	1	2	120	60.45	63.3
61	Trial (1)	1.5	2	120	63.89	63.0
62	Trial (2)	1.5	2	120	63.89	63.7
63	Trial (3)	1.5	2	120	63.89	64.0
64	Trial (1)	0.5	6.5	120	45.85	43.7
65	Trial (2)	0.5	6.5	120	45.85	43.0
66	Trial (3)	0.5	6.5	120	45.85	43.7
67	Trial (1)	1	6.5	120	49.30	47.0
68	Trial (2)	1	6.5	120	49.30	48.3
69	Trial (3)	1	6.5	120	49.30	46.7
70	Trial (1)	1.5	6.5	120	52.74	50.0
71	Trial (2)	1.5	6.5	120	52.74	47.0
72	Trial (3)	1.5	6.5	120	52.74	50.0
73	Trial (1)	0.5	9	120	39.66	40.3
74	Trial (2)	0.5	9	120	39.66	42.0
75	Trial (3)	0.5	9	120	39.66	44.0
76	Trial (1)	1	9	120	43.10	45.7
77	Trial (2)	1	9	120	43.10	46.7
78	Trial (3)	1	9	120	43.10	45.0
79	Trial (1)	1.5	9	120	46.54	49.7
80	Trial (2)	1.5	9	120	46.54	48.3

Observation	Replication	Dose	pH	Time	*Predicted %*	*Actual %*
81	Trial (3)	1.5	9	120	46.54	50.0

Appendix C-2: Experimental data of fluoride removal efficiency and adsorption capacity

Dose (g/L)	pH	Time (min.)	Replication	Removal Efficiency (%)	Adsorption Capacity(q_t) (mg/g)
0.5	2	60	Trial (1)	56.7%	34.0
0.5	2	60	Trial (2)	56.0%	33.6
0.5	2	60	Trial (3)	57.0%	34.2
1	2	60	Trial (1)	68.0%	20.4
1	2	60	Trial (2)	68.3%	20.5
1	2	60	Trial (3)	68.7%	20.6
1.5	2	60	Trial (1)	73.0%	14.6
1.5	2	60	Trial (2)	72.3%	14.5
1.5	2	60	Trial (3)	72.0%	14.4
0.5	6.5	60	Trial (1)	45.3%	27.2
0.5	6.5	60	Trial (2)	46.7%	28.0
0.5	6.5	60	Trial (3)	46.7%	28.0
1	6.5	60	Trial (1)	50.0%	15.0
1	6.5	60	Trial (2)	50.0%	15.0
1	6.5	60	Trial (3)	50.0%	15.0
1.5	6.5	60	Trial (1)	51.7%	10.3
1.5	6.5	60	Trial (2)	52.7%	10.5
1.5	6.5	60	Trial (3)	53.3%	10.7
0.5	9	60	Trial (1)	40.7%	24.4
0.5	9	60	Trial (2)	41.7%	25.0
0.5	9	60	Trial (3)	41.0%	24.6
1	9	60	Trial (1)	49.3%	14.8
1	9	60	Trial (2)	51.7%	15.5
1	9	60	Trial (3)	47.0%	14.1
1.5	9	60	Trial (1)	49.7%	9.9
1.5	9	60	Trial (2)	50.0%	10.0
1.5	9	60	Trial (3)	52.3%	10.5
0.5	2	90	Trial (1)	61.7%	37.0
0.5	2	90	Trial (2)	57.0%	34.2
0.5	2	90	Trial (3)	56.3%	33.8
1	2	90	Trial (1)	65.0%	19.5
1	2	90	Trial (2)	63.3%	19.0
1	2	90	Trial (3)	66.0%	19.8
1.5	2	90	Trial (1)	66.7%	13.3
1.5	2	90	Trial (2)	67.0%	13.4
1.5	2	90	Trial (3)	67.7%	13.5
0.5	6.5	90	Trial (1)	46.7%	28.0
0.5	6.5	90	Trial (2)	45.0%	27.0
0.5	6.5	90	Trial (3)	44.3%	26.6
1	6.5	90	Trial (1)	46.0%	13.8
1	6.5	90	Trial (2)	48.3%	14.5

Dose (g/L)	pH	Time (min.)	Replication	Removal Efficiency (%)	Adsorption Capacity(q_t) (mg/g)
1	6.5	90	Trial (3)	46.3%	13.9
1.5	6.5	90	Trial (1)	49.7%	9.9
1.5	6.5	90	Trial (2)	45.7%	9.1
1.5	6.5	90	Trial (3)	50.0%	10.0
0.5	9	90	Trial (1)	46.3%	27.8
0.5	9	90	Trial (2)	46.7%	28.0
0.5	9	90	Trial (3)	45.7%	27.4
1	9	90	Trial (1)	43.3%	13.0
1	9	90	Trial (2)	46.0%	13.8
1	9	90	Trial (3)	50.0%	15.0
1.5	9	90	Trial (1)	49.0%	9.8
1.5	9	90	Trial (2)	48.3%	9.7
1.5	9	90	Trial (3)	46.7%	9.3
0.5	2	120	Trial (1)	57.0%	34.2
0.5	2	120	Trial (2)	56.0%	33.6
0.5	2	120	Trial (3)	54.3%	32.6
1	2	120	Trial (1)	64.0%	19.2
1	2	120	Trial (2)	65.7%	19.7
1	2	120	Trial (3)	63.3%	19.0
1.5	2	120	Trial (1)	63.0%	12.6
1.5	2	120	Trial (2)	63.7%	12.7
1.5	2	120	Trial (3)	64.0%	12.8
0.5	6.5	120	Trial (1)	43.7%	26.2
0.5	6.5	120	Trial (2)	43.0%	25.8
0.5	6.5	120	Trial (3)	43.7%	26.2
1	6.5	120	Trial (1)	47.0%	14.1
1	6.5	120	Trial (2)	48.3%	14.5
1	6.5	120	Trial (3)	46.7%	14.0
1.5	6.5	120	Trial (1)	50.0%	10.0
1.5	6.5	120	Trial (2)	47.0%	9.4
1.5	6.5	120	Trial (3)	50.0%	10.0
0.5	9	120	Trial (1)	40.3%	24.2
0.5	9	120	Trial (2)	42.0%	25.2
0.5	9	120	Trial (3)	44.0%	26.4
1	9	120	Trial (1)	45.7%	13.7
1	9	120	Trial (2)	46.7%	14.0
1	9	120	Trial (3)	45.0%	13.5
1.5	9	120	Trial (1)	49.7%	9.9
1.5	9	120	Trial (2)	48.3%	9.7
1.5	9	120	Trial (3)	50.0%	10.0